LITHIUM AND NITROGEN IN METEORITIC MATTER

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in Partial Fulfilment of the Requirements
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DOCTOR OF PHILOSOPHY

By

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to the
DEPARTMENT OF CHEMISTRY
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21/12/81

CERTIFICATE

Certified that the work contained in this thesis entitled
'LITHIUM AND NITROGEN IN METEORITIC MATTER' has been carried out
by Mr. S.V.S. Suryanarayana Murty under my supervision and the
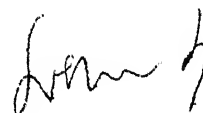same has not been submitted elsewhere for a degree.
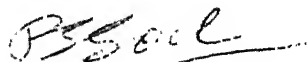
P.S. Goel
Thesis Supervisor

STATEMENT

I hereby declare that the research work embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur under the supervision of Professor P.S. Goel.

The extent of information derived from the existing literature has been indicated in this body of the thesis at appropriate places, giving the source of information.

(S.V.S. Suryanarayana Murty)

Statement verified

(P.S. Goel)
Thesis Supervisor.

(i)

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This is to certify that Mr. S.V.S. Suryanarayana Murty has satisfactorily completed all the course requirements for the Ph.D. degree programme in Chemistry. The courses include :

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Chm 521   Chemical Binding

Chm 523   Chemical Thermodynamics

Chm 524   Modern Physical Methods in Chemistry

Chm 541   Advanced Inorganic Chemistry I

Chm 543   Introduction to Nuclear Chemistry

Chm 600   Basic Course in Mathematics II

Chm 624   Valence Bond and Molecular Orbital Theories

Chm 626   Solid State Chemistry

Chm 642   Applications for Nuclear Chemistry

Chm 800   General Seminar

Chm 801   Graduate Seminar

Chm 900   Graduate Research

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ABSTRACT

Nitrogen and lithium have been measured by radiochemical
neutron activation analysis (RNAA) in bulk and separated
fractions of many stone and iron meteorites. In some cases
several other elements have also been studied.

Absence of serious contamination from atmospheric
nitrogen, has been demonstrated by devising a number of
experiments.

Irghizites and Muong Nong (M.N.) type tektites have been
studied for N,Li (by RNAA) and Fe, Cr, Co, Sc, Hf, Ta, Ce, Eu,
Tb and Cs (by INAA). N and Li in irghizites are like in other
tektite groups. Zhamanshinites have higher and variable N
and Li. Trace element contents of various layers of M.N. type
tektites show large variations. It appears that in the process
of glass formation in terrestrial environment N reaches an
equilibrium value of $\sim$ 20 ppm, provided the temperatures are
high. M.N. type tektites and Zhamanshine glasses did not
apparently reach the N equilibration temperature.

Li in ordinary chondrites is enriched in a HCl soluble
phase which is probably olivine. In the major silicate
minerals of ordinary chondrites Li is partitioned as :
$(Li)_{Olivine} > (Li)_{Plagioclase} > (Li)_{Pyroxene}$. A lighter
density fraction having high enrichments of N and Li has been
found in Allende and two ordinary chondrites.

N and Li have been studied in grain size separates of the magnetic and non-magnetic portions of a number of meteorites and enrichments have been observed in the fine grain fractions of some meteorites. Both N and Li enrichments could be due to the presence of a phase probably similar to the light density fraction of Allende. In Forest vale and Bjurbole N and Li enrichment has been observed in the fine fractions, similar to C. In Ambapur Nagla meteorite an unusually high N and Li enrichment has been observed in the finest magnetic fraction ($< 38\mu$).

N and Li have been studied in 19 iron meteorites. ^6Li contents range between 0.08 - 4 ppb with a large dispersion.

To understand the dispersion of N and ^6Li in iron meteorites, we have studied N and ^6Li in the phases separable by acid dissolution. We could isolate flakes (Taenite) magnetic residue (Schreibersite) and a small amount of non-magnetic residue (probably graphite and silicates) by dissolving a meteorite piece in dil. H_2SO_4. A very high enrichment of N and ^6Li in the non-magnetic residues has been found (N values are as high as 5000 ppm and ^6Li values as high as 1000 ppb).

The non-magnetic residue of iron meteorites has some other unusual and interesting features : (i) It has free radicals as measured by EPR, (ii) It has very high Xe contents and the isotopic composition is most unusual (measured by

Shukolyukov and Minh) (iii) Preliminary results show that it has Os of anomalous isotopic composition. These results, if confirmed, would suggest that some iron meteorites may contain presolar grains.

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CHAPTER 1

INTRODUCTION

Until recently, the solar nebula, from which meteorites and planets have formed by condensation and accretion, was believed to be homogeneous both chemically and isotopically (Larimer and Anders, 1967; Grossman and Larimer, 1974) as a result of complete mixing of atoms of diverse nucleosynthetic origin, either in interstellar space prior to formation of the nebula, or in the nebula itself prior to condensation. Recent observations have, however, shown that the nebula was not completely homogeneized as evidenced by the isotopic anomalies found in minor phases of primitive meteorites (Begemann, 1980). These minor phases are thought to be the relics of presolar material which have survived the solar system processing and have been preserved in some primitive meteorites (Anders, 1981).

Chemical and isotopic studies on separated phases of meteorites may prove rewarding in understanding the nebular processes and the heterogeneities in the solar nebula, which are very important for the understanding of the origin and evolution of the solar system. Nitrogen is one of the most abundant elements in the solar nebula (Trimble, 1975). But it has not been accreted to the extent as other elements, for example, carbon which is equally abundant in the nebula (Kung and Clayton, 1973). After noble gases, N is the most inert gaseous species

and hence anomalous N can be expected in those phases which have anomalous noble gases. Lattimer et al., 1978 predict anomalous N in E-chondrites on the basis of the scenario they presented for the origin of anomalous grains in meteorites. These considerations make N an interesting element for study.

The origin of light elements is still under dispute (Audouze and Vanclair, 1980). In particular the over-abundance of Li, Be and B in carbonaceous chondrites as compared to the Sun (Dwek, 1978; Reeves and Meyer, 1978) (See Fig. 1.1) has no satisfactory explanation. Various irradiation models proposed to account for the origin of certain isotopic ratios (Roberts et al., 1979; Clayton, 1979; Lee, 1978) are severely constrained by the effects they are required to produce in the light element systematics. Also the geochemical behaviour of Li in meteorites is not clear (Hutcheon et al., 1977). A study of Li abundances in separated phases of meteorites is therefore of considerable cosmochemical interest.

With these objectives in mind we have analysed N and Li in bulk and separated phases of stone and iron meteorites. A simultaneous study of N and Li isotopic compositions would have been more informative. But within our constraints we could only study the abundances.

In this chapter recent views on the classification of meteorites will be briefly summarised. The literature for the

relevant elemental and isotopic measurements will also be reviewed.

1.1 Meteorites and Classification

In the last decade the literature on meteorites has grown enormously and many new concepts have emerged. The Allende meteorite with its Ca-Al-rich inclusions, commands a special status in that, it has contributed greatly to most of our present knowledge of the early solar system chemistry. Reviews by Anders, 1964; 1971; Wasson, 1974; Sears, 1978a and Larimer, 1973 give an account of the important aspects of meteoritics.

Meteorites can be broadly classified into two classes. a) The undifferentiated meteorites in which there are again three types : Carbonaceous chondrites (having Fe in mostly oxidized form), enstatite chondrites (having Fe in mostly reduced form), and ordinary chondrites (having Fe in the intermediate state). b) The differentiated meteorite class which has three types :   achondrites, which are stone meteorites devoid of chondrules, iron meteorites which are mostly Fe + Ni alloy, and stony-irons, which are roughly a mixture of irons and achondrites having intergrowth of metal and silicate.

1.1.1 Carbonaceous Chondrites : These meteorites are supposed to be the most unaltered material from the primary condensates of the solar nebula, and as such represent the solar nebula in

their chemical composition. Recent classification divides
this group into four subgroups as follows : CI (high
volatile content and no chondrules) CM (intermediate volatile
abundances and small chondrules $\sim$ 0.2 mm) CO (low volatile
abundances and small chondrules) and CV (low volatile
abundances and large chondrules $\sim$ 1 mm) (VanSchmus, 1969;
VanSchmus and Hayes, 1974; McCarthy and Ahrens, 1972; Kallemeyn
and Wasson, 1979). CI is the most primitive of the above four
classes whose elemental abundances, originally used by Suess
and Urey, 1956 to calculate the solar abundances of elements,
have since been improved by Cameron, 1973 and Trimble, 1975.
A comparison between CI and solar abundances is shown in
Fig. 1.1(from Holweger, 1977).

1.1.2 <u>Ordinary Chondrites</u> : This class is divided into three
groups, based on their metal content, denoted by the letters
H (high iorn), L (low iron) and LL (low iron, low metal) to
denote the group, followed by an arabic number 3-6 to denote
the increased degree of metamorphism, type 3 being the un-
equilibrated and least metamorphosed (VanSchmus and Wood,
1967). Thermoluminescence sensitivity (TLS) (Sears et al.,
1980) and distribution of Co and Ni in kamacite (Afiattalab
and Wasson, 1980) have been used as measures of the extent of
unequilibration in type 3-chondrites. Chemical and petrological
studies of the U.O.C. (unequilibrated ordinary chondrites)
matrices (Huss et al., 1981) indicate these to be a low
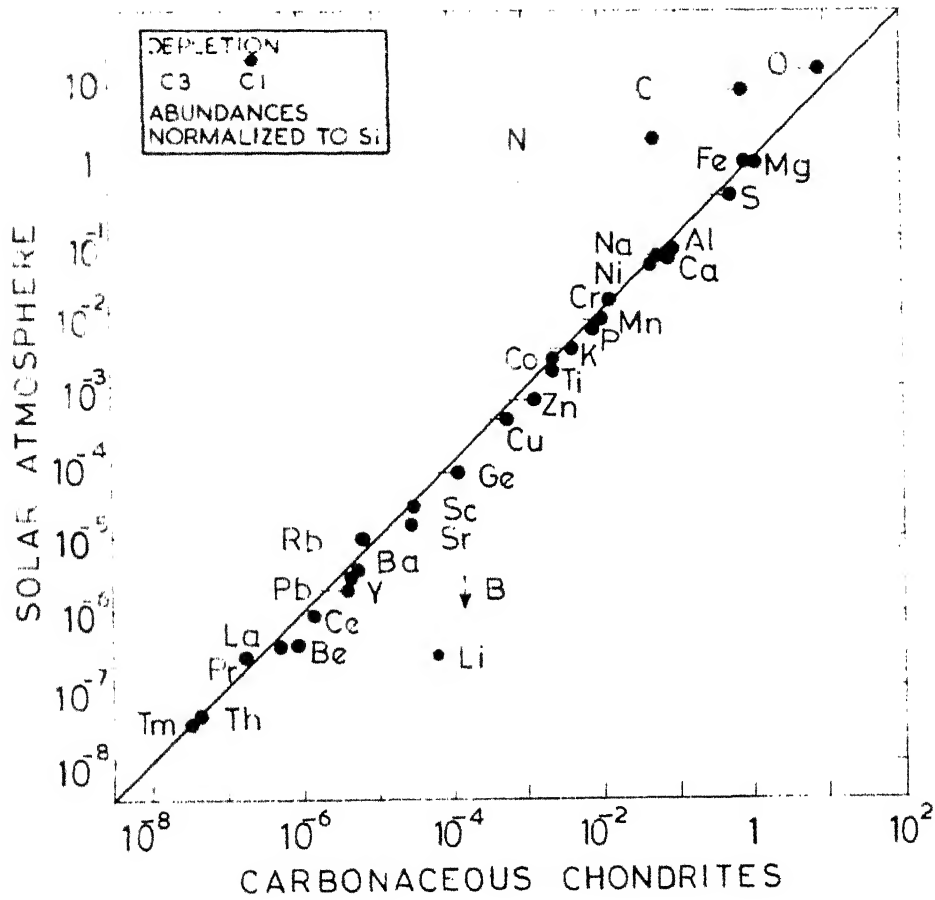
Fig.1.1 Comparison of C1 and Solar abundances (from Holweger,1977)

temperature condensate as proposed by Larimer and Anders
(1967; 1970). A group of ten H (3-6) chondrites have been
studied by a consortium to gain a better understanding on
their mineralogical, petrological and chemical composition
and to try to understand their formation-history (Turner et al.,
1978; Hertogen et al., 1977; Ashworth, 1980, 1981; Christophe
Michel-Levy, 1981; Hutchison et al., 1980, 1981).

1.1.3 <u>Enstatite Chondrites</u> : Among chondritic groups, enstatite
chondrites are unique for their extreme degree of reduction and
their mineralogy. They consist of almost pure enstatite, metal,
sulphides and minor amounts of olivine, plagioclase and
clinopyroxene (Keil, 1968; Mason, 1966). The sulphide mineralogy
is complex. Elements which are strongly lithophile in ordinary
chondrites (Ca, Cr, Ti, Mg, Mn and K) occur in sulphide phase
in enstatite chondrites (Keil, 1968). The most intriguing
property of this chondrite group is that major chemical differen-
ces exist between the petrologic type 4,5 and 6 (Keil, 1968;
Baedecker and Wasson, 1975; Sears, 1980). The higher content of
volatile elements (Tl, Bi, In, Cd etc.) of E4 ,5 as compared to
E6 is an indication that accretion occurred during cooling of
the solar nebula, with E6 chondrites forming at higher tempera-
tures (Rambaldi and Cendales, 1980). A region in the solar
nebula where the C/O ratio was somewhat greater than the solar
value (Larimer and Bartholomay, 1979); or solar composition and
a total pressure of $\sim$ 1 atm., provided that thermodynamic

equilibria are frozen in,at near-formation temperatures
(Herndon and Suess, 1976),have been suggested as the locales
for the formation of E-chondrites.

1.1.4 <u>Achondrites</u> : Some of the achondrites are unique and
require separate classification for each case. But in
general two classes can be distinguished on the basis of Ca
content (Wasson, 1974). The Ca-poor variety appears to be
more closely related chemically to chondritic meteorites.
These include : aubrites (enstatite achondrites) ureilites
and diogenites. Aubrites are highly reduced and resemble
E-chondrites, except that metal and sulphide are missing.
Ureilites consist of olivine, pyroxene and a few Ni-poor
($\sim 2\%$) metal grains plus one percent carbon in the form of
graphite and diamonds. (Wlotzka, 1972; Ramdohr, 1972;
Berkley et al., 1980). The dominant mineral in diogenites is
hypersthene (Duke and Silver, 1967).

The most common type of achondrites are the Ca-rich
eucrites and howardites. Eucrites resemble terrestrial and,
to an even greater extent, lunar basalts (Anders, 1977). They
normally contain pyroxene and plagioclase feldspar. Though
almost all achondrites are brecciated (Wasson, 1974),howardites
represent an extreme case.

1.1.5 <u>Iron Meteorites</u> : This class of meteorites contain
chiefly Fe ($\sim 90\%$) and Ni ($\sim 10\%$) with Co, P and S in

minor amounts (< 1 %). The key parameters for classifying
iron meteorites into genetic groups are concentration of Ga
and Ge. Their taxonomic value results from the combination
of a very wide concentration range in iron meteorites as a
whole, with very narrow concentration ranges in most individual
groups. (Wai and Wasson, 1979). Recent calculations show that
the nebular condensation temperature of Ge is lower than that
of any other siderophile and that Sb and Ga are the next most
volatile siderophiles (Wai and Wasson, 1977). The narrow
intragroup ranges of Ga and Ge reflect minimal fractionation
during the crystallisation of cores (Wai and Wasson, 1979).

Although the total concentration ranges among all
meteorites vary by large factors for Ga and Ge, only the two
groups IAB and III CD have Maximum/Minimum > 2. There is
evidence which indicates that the groups having wider ranges
may have been established during nebular fractionation
(Wasson, 1970; Scot and Bild, 1974) or partial melting process
(Kelly and Larimer, 1977).

Presently, the iron meteorites are classified into 13
groups, principally defined by their Ga, Ge and Ni contents
(Kracher et al., 1980). Eleven of these are believed to have
formed by the fractional crystallization of planetary cores.
Evidence for this comes from their chemical fractionation
trends, the absence of chondritic silicates and the large

size of precursor taenite grains (Wasson, 1972; Scot and
Wasson, 1975). These groups were earlier called 'igneous'
and are now referred to as 'magnetic' groups. The other two
groups — IAB and III CD, may have formed in a body of chondri-
tic composition as individual pools of shock melt, varying
systematically in their relative amounts of metal and sulphides
(Wasson et al., 1980). Sears (1978b) calculated the pressure
and temperature conditions in the primordial nebula which
could produce the observed Ni, Ga and Ge abundances in the
major iron meteorite groups, assuming equilibrium condensation.
He arrived at a temperature range of $600-750^{\circ}K$ for all iron
meteorite parent bodies but a very wide range of pressures,
10^{-4} atm. for I AB and II AB; $5x10^{-6}$ for III AB and 10^{-8} for
IV A and suggested (Sears and Axon, 1977; Sears, 1979) the
orbits of Venus and Earth (for I AB) asteroid belt (for III AB)
and the orbit of Saturn or beyond (for IV A) as the formation
sites for these major groups of iron meteorites.

1.1.6 <u>Inclusions in iron meteorites</u> : Iron meteorites contain
three types of gross inclusions; troilite, graphite and silicate.
Graphite occurs as centimeter-sized nodules in association with
troilite and silicates in group I and I - Anomalous irons. Out-
side these groups graphite nodules are rare or absent. Fine
graphite lamellae and spherulites, that usually are the decompo-
sition products of former carbides, occur in groups II A, II D,
III D, III E and several anomalous irons. Silicate inclusions

are frequent in IAB and II E groups mostly. There are
17 instances of silicate-bearing meteorites among the 92
anomalous irons. Out of 293 iron meteorites belonging to the
rest of iron meteorite groups only 6 instances of very minor
silicate inclusions were found (Buchwald, 1975).

Troilite and graphite inclusions : While the troilitic sulphur
has the same isotopic composition in iron meteorites the graphitic
carbon is enriched in the lighter isotope to varying extents in
different iron meteorites (Deines and Wickman, 1973). Iron
meteorites also contain free carbon which lacks the characteri-
stic properties of graphite. It may be amorphous (Mason, 1962).
This carbon had further enrichment of light isotope ($\delta^{13}C$ upto
-24.75 ‰) as compared to -4.8 to -8.2 ‰ for inclusion graphite).
(Deines and Wickman, 1973). Fig. 1.2 (from Deines and Wickman,
1973) describes the $\delta^{13}C$ for graphitic carbon of iron meteorites.

Silicate inclusions : Bunch et al., 1970 have studied the
mineralogy and petrology of the silicate inclusions from IAB
and II E irons and found them to be chondritic. Bulk chemical
analyses have been published for inclusions from Woodbine
(Jarosewich, 1967) Landes (Kracher, 1974) and Campo del Cielo
(Wlotzka and Jarosewich, 1977). These authors have pointed out
that the major elements occur in the inclusions at the same level
as in chondrites.

The angular shape of the silicate inclusions, the presence
of chondrules in Netschaëvo inclusions (Bunch et al., 1970) the
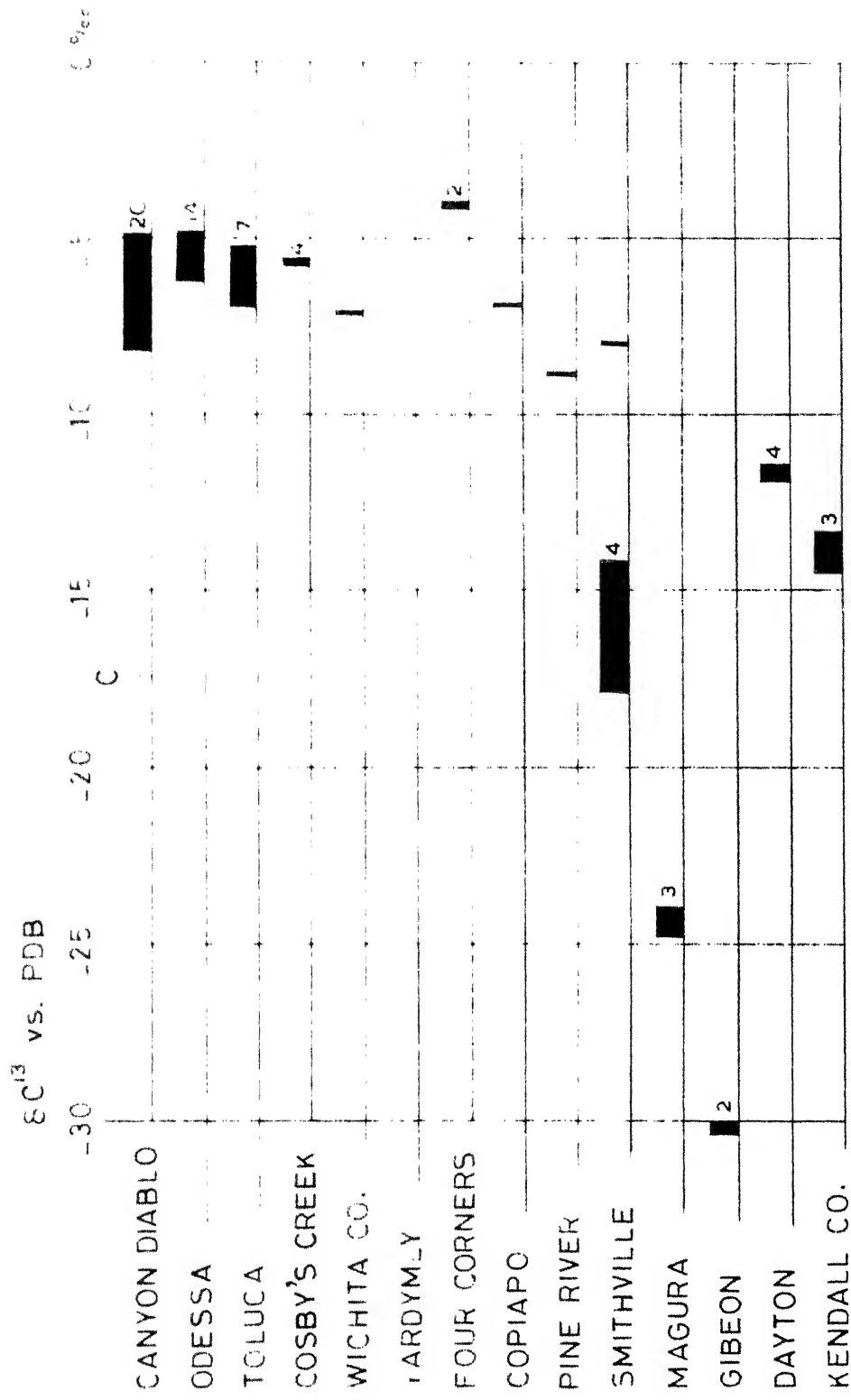
Fig.1.2   Carbon isotopic variations in iron meteorites. C = Cohenite,
number of measurements are indicated (from Deines and
Wickman,1973).

Rb-Sr and K-Ar ages which are around 4.5 AE (Burnett and Wasserburg, 1967; Bogard et al., 1968; Niemeyer, 1979a), the excess ^{129}Xe which correlates with ^{127}I (Alexander and Manuel, 1967; Niemeyer, 1979b, 1980) the presence of planetary noble gases (Bogard et al., 1971; Hintenberger et al., 1969) and their chondritic composition with unfractionated REE pattern (Bild, 1977a,b) all point towards the antiquity of these silicate inclusions.

Two types of silicate inclusions have been identified from IAB irons. The first group (Copiapa, Landes and Woodbine) have chondritic abundances and the second group (Campo del Cielo and Mundrabilla) have undergone metal silicate fractionation (Robinson and Bild, 1977). Two types of silicate inclusions have also been found from IIE group, based on their K-Ar ages (Niemeyer, 1980). One group has an age of 4.5 AE while the other has a much younger age of 3.8 AE.

1.2 Trace Elements in Meteorites

In this section,N and Li in meteorites and noble gases in the inclusions of iron meteorites,will be discussed.

1.2.1 Nitrogen : Nitrogen is one of the most abundant elements after H and He, in the solar nebula. It has two stable isotopes ^{14}N and ^{15}N. ^{14}N is synthesized mostly from ^{12}C and ^{16}O through H burning in the stellar envelopes by the CNO equilibrium process, while ^{15}N is destroyed in this process

(Penzias, 1980). Non-equilibrium or explosive H burning
(Audouze, 1977) (as in nova explosions) is regarded as the
most likely source of ^{15}N. In the solar nebula nitrogen is
expected to be present dominantly in the molecular form,
even at low temperatures, and ammonia could at the most
account for only 3% nitrogen (Norris, 1980).

Nitrogen in Meteorites : In spite of its high abundance in
the solar nebula, nitrogen has not been accreted to that
extent in stone as well as iron meteorites (Gibson, 1969;
Gibson and Moore, 1971a,b; Moore, 1971; Gibson et al.,1971a;
Kothari, 1974; Kothari and Goel, 1974; Shukla, 1977; Shukla
and Goel, 1981; Kung and Clayton, 1978). The higher abun-
dance of N in carbonaceous and enstatite chondrites (Gibson
et al., 1971b; Moore et al., 1969) is due to the presence
of organic compounds and inorganic nitrides (TiN and Si_2N_2O)
respectively (Bannister, 1941; Anderson et al., 1964). On
the basis of the observation that in E-chondrites TiN has
been observed only in chondrules while Si_2N_2O appears res-
tricted to the matrix only, along with SiO_2, and thermodynamic
constraints Larimer et al., 1980 proposed a secondary origin
for Si_2N_2O, probably during metamorphism. The presence of
Carlsbergite (CrN) (Buchwald and Scot, 1971) in some iron
meteorite groups (chiefly in III A and occasionally in IA and
II A : Scot, 1973) might have been responsible for the occa-
sional higher abundances of nitrogen in iron meteorites.

1.2.2 _Light elements_ : The light elements D, ^{6}Li, ^{9}Be, ^{10}B and ^{11}B (and possibly ^{7}Li) are not produced by the general nucleosynthetic processes occurring in stars (Bulbridge et al., 1957). They appear to be synthesized by high energy processes occurring either during the interaction of G.C.R. with the interstellar medium or in supernovae envelopes (Audouze et al., 1976; Audouze and Vanclair, 1980). The bulk of ^{7}Li ($\sim$ 90%) is likely to be produced in the 'Big Bang' (Schramm and Wagoner, 1977). For the remaining ^{7}Li, diverse astrophysical environments like red giants (Canal et al., 1977) nova explosions (Starfield et al., 1978) supernova shocks (Epstein et al.,1976) and cosmic ray spallation on interstellar matter (Reeves, 1974; Meneguzzi and Reeves, 1975) have been proposed. But these sources do not seem fully capable of providing the galactic requirements for ^{7}Li and the origin of ^{7}Li remains poorly understood (Starfield et al., 1978).

1.2.3 _Lithium in Stellar Atmospheres_ : Lithium content of various stars differs by more than a factor of 10^{6}. Colder stars have lower Li content. Also in young stars the Li content is greater than in old stars (Boyarchulk, 1976). Li in red-giants is almost 100 times the meteoritic value, implying that Li in these stars must come from some kind of local synthesis (Canal et al., 1977). In most of the stars ^{6}Li is not found. Magnetic variable stars with ^{6}Li/^{7}Li in the range 0.10 - 2.00 are an exception (Boyarchulk, 1976).

1.2.4 <u>Lithium in Meteorites</u> : Li, Be and B are enriched in carbonaceous chondrites as compared to the solar photosphere (See Fig. 1.1). The CC abundances of Li (Quijano-Rico and Wänke, 1969; Nichiporuk and Moore, 1970, 1974) are much higher compared to galactic abundance. The recent values of B (Weller et al., 1978; Curtis et al., 1980) and Be (Vilcsek, 1977) are also very high in CC as compared to the galactic abundances (Reeves and Meyer, 1978). Dwek, 1978 proposes the presence of irradiated graphite grains in meteorites. The lower solar abundances are due to the fact that no graphite grains bearing Li, Be, B are present in the Sun, which points towards a distinct nuclear origin for Li, Be, B in the graphite grains, probably cosmic ray bombardment in the interstellar medium.

Li in stone meteorites has been studied by a number of workers (Pinson et al., 1953; Shima and Honda, 1963, 1966, 1967a; Krankowsky and Müller, 1964, 1967; Quijano-Rico and Wänke, 1969; Nichiporuk and Moore, 1970, 1974; Hutcheon et al., 1977; Phinney et al., 1979; Shukla, 1977). In ordinary chondrites Li values are 1-3 ppm. In achondrites Li ranges between 1 to 10 ppm, being highest in eucrites. This enrichment is due to the chemical differentiation of Li during the formation of achondrites, and its lithophile character. But in E-chondrites Li behaves as a chalcophile (Nichiporuk and Moore, 1970) just like the other conventional lithophiles (Mg,Ca etc.) behave in E-chondrites (Keil, 1968).

There are only two reports till now on Li in iron meteorites (Fireman and Schwarzer, 1957; Krankowsky and Müller, 1967), probably due to the difficulty in measuring the ppb amounts of Li in iron matrix.

Condensation behaviour of Lithium : The gaseous form of Li is the atomic Li (g). Since the ionic radius of Li^+ (0.68 Å) is close to Mg^{2+} (0.65 Å), substitution of Li^+ for Mg^{2+} in silicates is expected (Wai and Wasson, 1977). Shima and Honda, 1967a showed that Li in ordinary chondrites is in a phase soluble in HCl, probably olivine, while the other alkali metals are in other phases. Li was tentatively classified as a refractory element by Ganapathy and Anders, 1974, while Dreibus et al., 1976 found no Li enrichment in one coarse grained Allende inclusion. Absence of Li from the major minerals of Allende inclusions has been reported by Hutcheon et al., 1977. They conclude that Li is not a refractory element and it is concentrated either at grain boundaries or in late (?) uncharacterized mineral phase.

1.2.5 Noble gases in iron meteorite inclusions : Light noble gases (He, Ne and Ar) have been investigated in iron meteorite inclusions by (Begemann, 1965; Alexander et al., 1968; Fireman and De Felice, 1968; Levskey and Komarov, 1975) and in separated phases of iron meteorites (Taenite and Schreibersite) by Schultz et al., 1969, 1971. The main conclusions are : 1) the

results for cosmogenic isotopes of He, Ne and Ar disagree appreciably with data on accelerator irradiated targets 2) the ratio $^4He/^3He$ in the inclusions ranged from 6.70 to 30.5 as compared to the value 3.85 to 4.65 in the metal phase. 3) excess ^4He of unknown origin was observed in troilite inclusions, 4) some inclusions have lost considerable amounts of gas by diffusion, 5) the ^3He concentration in taenite were lower than those in either schreibersite or bulk samples. This difference cannot be attributed solely to variation in the chemical composition and is contradictory to observations of hydrogen diffusion in kamacite and taenite.

The heavy noble gases have also been studied by a number of workers. These studies have led to the following observations : 1) Distinct excess of ^{129}Xe has been observed in several phases, troilite (Reynolds et al., 1962; Alexander et al., 1968) graphite (Alexander and Manuel, 1967; Fireman and De Felice, 1968) and silicate (Alexander and Manuel, 1968; Hintenberger et al., 1969), 2) concentrations of 'trapped' Xe and Kr are within the relatively large range found in chondrites (See Marti, 1967). However, the Xe data from Toluca silicate (Alexander and Manuel, 1968) require the presence of a trapped component which is isotopically distinct from the atmosphere 3) excesses of $^{80,83}Kr$ and $^{128,131}Xe$ in troilite/and graphite were attributed to neutron capture reactions on Br, Se and Te (Clarke and Thode, 1964; Alexander and Manuel, 1967;

Alexander et al., 1968; Fireman and De Felice, 1968), 4) Kr
and Xe (except ^{129}Xe) showed a grain size dependence. This
indicates that ^{129}Xe has no relation with residual Xenon
(Hintenberger et al., 1969), 5) The inclusions in Lindwood are
peculiar. Silicate Xe data are a mixture of atmospheric Xe
and a small amount of spallation. No AVCC Xe appears to be
present. But the silicate Kr data required the presence of
AVCC Kr. On the other hand the graphite contains atmospheric
Xe with an admixture of AVCC or an unusual spallation compo-
nent (^{130}Xe/^{128}Xe = 1.5). (Bogard et al., 1971). Although
preferential adsorption of atmospheric Xe in variable amounts
(Alexander and Manuel, 1967) could explain the Lindwood iso-
topic data ^{84}Kr/^{132}Xe ratio gave no indication of this
(Bogard et al., 1971).

1.3 _Isotopic Anomalies in Meteorites_ : The concept of a
homogeneous solar nebula has turned out to be erroneous in
recent times (Manuel and Sabu, 1975, 1977; Sabu and Manuel,
1976a,1980a; Boynton, 1978a,b; ElGoresy et al., 1978; Manuel,
1979, 1980; Grossman, 1980). Anomalies have been discovered
in the isotopic composition of a number of elements which cannot
be explained by processes known to be going on within the solar
system at present. They appear to reflect primordial heteroge-
neities, testifying to variations in space and/or time of the
isotopic composition of these elements within the protosolar
nebula. They contribute to our understanding of processes and

of time scales in the early solar system, before and after its
formation. Some reviews on this topic are : Reeves (1978);
Black (1978); Podosek (1978); Clayton (1978); Schramm (1978,
1980); Clayton D.D. (1979); Hillebrandt (1979); Lee (1979);
Begemann (1980); Symbalisty and Schramm (1981); Lavrukhina (1980).

Till to date isotopic anomalies have been reported in about
one third of the elements covering the periodic table, and more
elements are being added to the list. Isotopic variations can be
categorized in terms of fractionation, creation and destruction
of isotopes via nuclear reactions with energetic particles in
the solar system, decay of primordial radionuclides, and pre-
solar nebular heterogeneities. Fig. 1.3 (from Black, 1978)
gives a schematic representation of the processes that might
have contributed to the history of various isotopes in the
present solar system. The isotopic anomalies, other than those
produced by cosmic ray spallation are summarized in Table 1.1,
where the type of anomaly, the material where it was observed
and the most probable cause of the anomaly are given. The
isotopic anomalies for the elements N, Li, Xe and Kr will be
briefly reviewed here.

1.3.1 <u>Nitrogen</u> : Different groups of stone meteorites have
significantly different isotopic compositions of N (Kung and
Clayton, 1978; Frick and Pepin, 1980; Robert and Epstein, 1980;
Thiemens and Clayton, 1980) although the actual nature of the
relationship between $^{15}N/^{14}N$ and chemical petrological
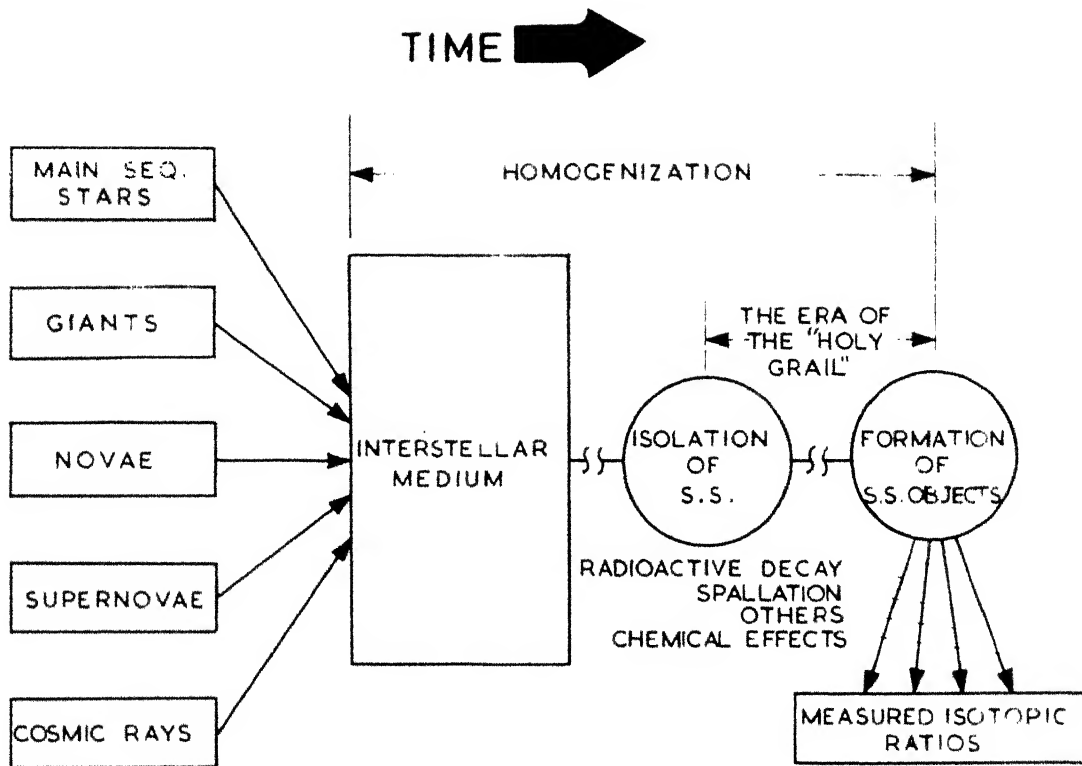
Fig.1.3   Isotopic history of the present-day solar system (from Black, 1978)

Table 1.1 Summary of the isotopic anomalies observed in
meteorites

Element	Type of anomaly	Where observed	Most probable cause
D	Highly variable D/H	CC* and Chainpur	Physico-chemical processes or early irradiation.
Li,Be,B	Expected	-	Mode of synthesis of these elements
Li	Excess ^{7}Li	Kirin[1]	-
	Excess ^{6}Li	Iron meteorites[2]	Cosmic-ray spallation(?)
C	Variable ^{13}C/^{12}C	CC and other meteorites also	Physico-chemical processes
	Excess ^{12}C	Carbon residue of iron meteorites[3]	Fossil carbon
N	Variable ^{15}N/^{14}N	Stone meteorites	Physico-chemical processes or nuclear effects
	Excess ^{14}N	Carbon residue of Allende[4]	Nuclear effects (?)
O	Excess ^{16}O	Allende and Leoville Inc.	Presolar grains carrying pure ^{16}O
Ne	Excess (pure)^{22}Ne	Minor (C-rich) phases of CC	Extinct ^{22}Na(decayed to ^{22}Ne) carried by presolar grains
Mg	Excess ^{26}Mg	Allende and Leoville Inc.	Extinct ^{26}Al
	Excess ^{25,26}Mg and depleted ^{24}Mg	C1, EK-1-4	FUN[a]

Table 1.1 (contd...)

Element	Type of anomaly	Where observed	Most probable cause
Si	Excess heavy isotopes	C1,EK-1-4	FUN
S	Slight excess of ^{33}S	Allende residue	Neucleo synthetic heterogeneity
Ar	Excess ^{40}Ar	Allende Inc.	Interstellar grains carrying excess ^{40}Ar (due to ^{40}K decay)
	Excess ^{40}Ar	Iron meteorites[5]	A primordial terrestrial like Ar
Ca	Excess ^{42,48}Ca	C1, EK-1-4,HAL	FUN
Ti	Excess ^{47,49,50}Ti	C1,EK-1-4	FUN
	-do-	Allende Inc.[6]	Nucleosynthetic heterogeneity
V	Excess ^{50}V expected (But not observed)	Gas-rich meteorites	Irradiation effects
Cr	Excess heavy isotopes	Taenite phase of iron meteorites[7]	Diffusion (probably presolar(?
Kr	Depletion of ^{78,80}Kr	Allende acid residue	Not clear
Sr	Excess ^{86,87,88}Sr	C1,EK-1-4	FUN
Ag	Excess ^{107}Ag	IV A irons	Extinct ^{107}Pd
Cd	Excess heavy isotopes	Tieschitz and Brown field[8]	Rayleigh distillation process in the early solar system
Te	Excess p-and r-isotopes	Carbon residue of Allende	Supernova synthetic products
	Excess s-isotopes	Spinel residue of Allende	-do-

Table 1.1 (contd...)

Element	Type of anomaly	Where observed	Most probable cause
Xe	Excess ^{129}Xe	Most of solar system materials	Extinct ^{129}I
	Excess β-unshielded isotopes	-do-	Extinct ^{244}Pu
	CCFXe(Excess p-and r-isotopes)	Acid resistant carbonaceous phase of meteorites	Extinct SHE+Fractionation or supernova r- and p-products
	Xe-s (Excess s-isotopes)	A minor phase of Murchison	Grains from red-giants
	Depletion of 124,126$_{Xe}$ (This work)	Iron meteorite residues	Presolar grains(?) (See Chapter 5)
Ba	Excess ^{135,137}Ba	C1,EK-1-4	FUN
Nd	Excess r-isotopes	C1,EK-1-4	FUN
Sm	-do-	-do-	FUN
Os	Expected (Not found)	In primordial metal grains	Nuclear heterogeneity
Hg	Excess ^{202}Hg or depletion of 196$_{Hg}$	Ordinary as well as CC	Extinct ^{202}Pb or deficiency in p-nuclides
U	Excess ^{235}U	Ordinary meteorites	Extinct progenitors

[*] Carbonaceous condrite; [a]. FUN = Fractionation and unknown nuclear.
1. Li (1977); 2. Brick and Allegre (1980); 3. Deines and Wickman(1973);
4. Kung and Clayton (1978); 5. Hennecke and Manuel (1977); 6.Niemeyer
and Lugmair (1981); 7. Shima and Honda (1965); 8. Rossman et al.,
(1980); (Information for the rest of the anomalies is derived from
the reviews cited in the text).

classification is unclear (Kerridge, 1980). Kung and Clayton, 1978 have recognized four major isotopic groups, 1) C1 and C2 carbonaceous chondrites have $\delta^{15}N$ of +30 to +50‰ (with one large anomaly, Renazzo has $\delta^{15}N$ of +170‰); 2) enstatite chondrites have $\delta^{15}N$ of -30 to -40‰ ; 3) C3 chondrites have low $\delta^{15}N$ with large internal variations; 4) ordinary chondrites have $\delta^{15}N$ of -10 to +20‰. Fig. 1.4 shows these four groups on a N vs $\delta^{15}N$ plot. (From Kung and Clayton, 1978). The major variations are primary, representing isotopic abundances established at the time of condensation and accretion. Secondary processes such as spallation reactions, solar wind implantation and metamorphic losses may cause small but observable isotopic variations in specific cases (Kung and Clayton, 1978). A high enrichment of ^{15}N in solar wind nitrogen in lunar samples (Becker et al., 1976; Becker and Clayton, 1977a)has no clear explanation (Kerridge et al., 1977). A very high enrichment of 75% of ^{15}N in the atmosphere of Mars has been attributed to extensive mass fractionation (McElroy et al., 1976). Apparently formation of organic matter in carbonaceous chondrites and inorganic nitrides in enstatite chondrites favoured heavy and light isotopes respectively (Kerridge, 1980), but the fractionation during Fischer-Tropsch synthesis cannot account for the large fractionations observed (Kung et al., 1979). Temporal or spatial variations in the isotopic composition of nitrogen in the solar nebula or nuclear processes (Kung et al., 1979;
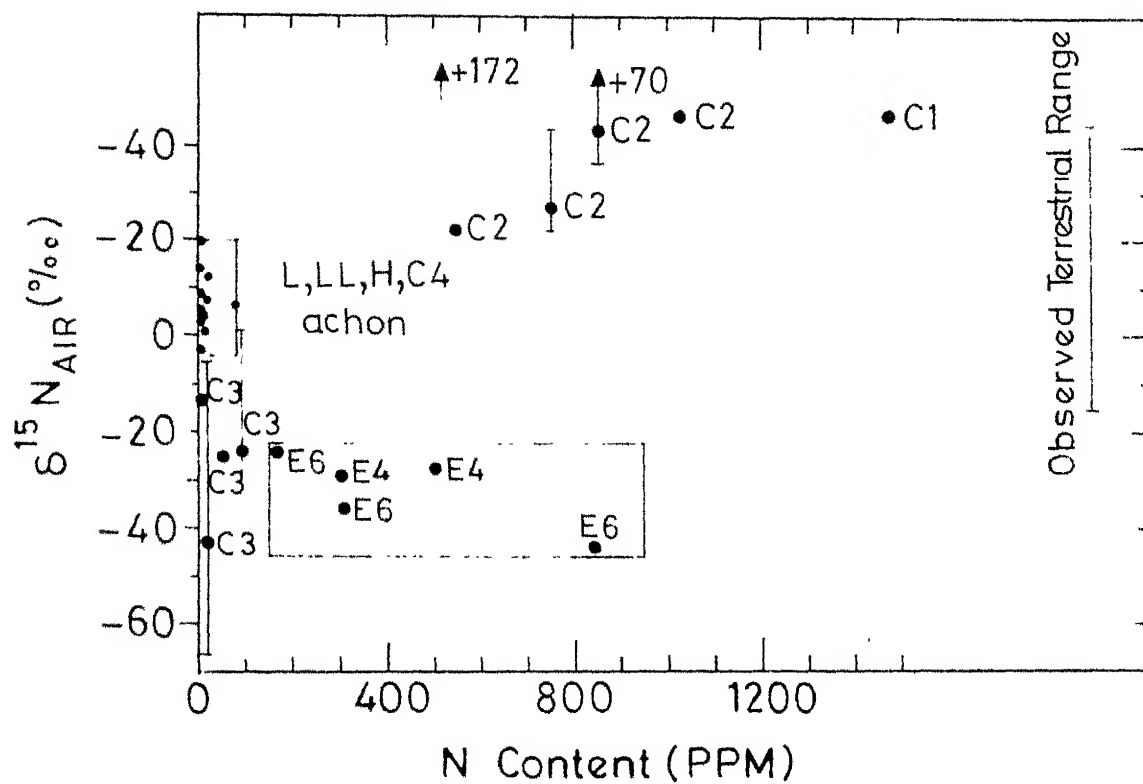
Fig.1.4 Nitrogen abundances and isotopic
compositions of stone meteorites
(from Kung and Clayton,1978)

Frick and Pepin, 1980) may be the plausible explanations.

1.3.2 <u>Lithium</u> : At least two sources are required to account for the ^{7}Li in the solar system, one being the 'Big Bang'. Depending upon the contribution from the other source, the region of space in the solar system, and the time of condensation, the isotopic ratio of Li is expected to vary (Rajan et al., 1980). The early report of large variations in the Holbrook meteorite (Poschenrieder et al., 1965) has been discounted as instrumental error (Gradsztajn et al., 1968). But the work of Bernas et al., 1969 clearly indicates a $\pm$ 10 % variation in the ratio for Holbrook and other ordinary chondrites. These authors attribute this to the neutron irradiation effect, as suggested by Fowler et al., 1962 which consumes ^{6}Li. Recently, Li, 1977 has reported ^{7}Li/^{6}Li ratios of 17.3 $\pm$ 1.2 in the Kirin meteorite, an excess of 42% over terrestrial samples. The work on other meteorites (Balsiger et al., 1968; Dews, 1966; Krankowsky and Müller, 1967; Brick and Allegre, 1980; Phinney et al., 1979) and even the anomalous Ca-Al-rich inclusions of Allende (Rajan et al., 1980; Klossor et al., 1981) indicated ^{7}Li/^{6}Li ratio within $\pm$ 2% of terrestrial value. The constancy of Li isotopic ratio is incompatible with the theories on origin of Li. May be further reduction in sample size ($\ll$ 1 mg) will reveal the hetrogeneities in the ^{7}Li/^{6}Li ratio, which are otherwise masked in large samples.

Li in iron meteorites has been shown to have $^7Li/^6Li$ ratio of 1-2 (Levisky et al., 1972). Recently, Brick and Allegre, 1980 found a value of 5.3 for Grant meteorite. Cosmic ray irradiation effects have been proposed as the reason. But cosmic ray spallation will be inadequate to produce measurable changes in the $^7Li/^6Li$ ratio of the original Li in iron meteorites (see Chapter 5 for details).

1.3.3 <u>Importance of noble gases</u> : The chemical heterogeneity that existed prior to condensation was in many cases obscured by chemical separation of elements into different minerals during condensation. However, a few elements with very similar chemical properties have retained a record of the chemical heterogeneities that existed prior to the redistribution of elements during condensation. The five inert gases have similar physical properties and are essentially inert to chemical reactions. It is not surprising then, that these elements provided the first clear evidence of chemically and isotopically distinct regions in the primitive nebula.

Meteoritic noble gases are a mixture of various components consisting of 1) A trapped component at the time of condensation of grains from the nebula 2) An implanted component such as from solar wind, best preserved in lunar soils (Pillinger, 1979), 3) a spallogenic component due to cosmic ray bombardment 4) a fissiogenic component from the spontaneous fission of U and Th 5) a radiogenic component from the decay of now extinct

nuclides like ^{129}I, ^{244}Pu and possibly extinct super-heavy elements (SHE) and 6) a component carried by the presolar grains. It is fortunate that these various components reside at different sites which have different thermal retentivities and different resistivities to chemical attack by various acids. A combination of differential chemical attack and a step-wise heating technique has made it possible to separate each noble gas into its various components.

1.3.4 <u>Krypton and Xenon</u> : Xenon has turned out to be perhaps the most prolific single element to study, the reasons being 1) Xe has 9 stable isotopes, covering in atmospheric Xenon a wide range of abundances from about 0.1% for $^{124,126}Xe$ to 27% for $^{129,132}Xe$ 2) It is depleted in meteorites by atleast five orders of magnitude. Consequently if for Xe and any of its neighbours effects of comparable absolute magnitude are produced, after this depletion has occurred, then the relative anomalies will be correspondingly higher for Xenon. 3) Aside from $^{129,131,132}Xe$ which are mixtures of s- and r- products, there are isotopes which are pure p- (124,126) pure r-(134,136) and pure s-products (128,130).

Reynolds and Turner, 1964 have found in carbonaceous chondrites a component of Xenon enriched in the heavy isotopes 131-136. They have given it the acronym CCFXe (carbonaceous chondrite fission Xenon). This has been attributed to the

fission of a SHE in the meteorite (Srinivasan et al., 1969;
Anders and Heymann, 1969; Dakowski, 1969). This interpretation
has been questioned by (Manuel et al., 1972; Sabu et al., 1974)
since the excess heavy isotopes are always accompanied by an
excess of the light β-shielded isotopes of 124-128 which cannot
be made by fission. Alternative explanations have been proposed
according to which the light and heavy components were made in
a supernova and were then trapped in solid grains which even-
tually found their way into the meteorite (Manuel et al., 1972;
Sabu and Manuel 1976b;Black 1975; Howard et al., 1975; Clayton,
1975, 1976).

In an attempt to separate the phase where the CCFXe has
been concentrated, the Chicago group has embarked upon a pro-
gramme of selective dissolution of minerals by a variety of
acids (Srinivasan et al., 1975; Lewis et al., 1975; 1976; 1977).
In the C3V meteorite Allende,2/3 of the noble gases turned out
to reside in an HF-HCl insoluble residue, comprising only 0.5%
of the meteorite and dubbed as 'Q' phase. This is shown to be
true for other carbonaceous chondrites (Srinivasan et al.,
1977; Frick and Moniot, 1977; Reynolds et al., 1978; Alaerts
et al., 1979a, 1980) and also for ordinary chondrites
(Moniot, 1980; Alaerts et al., 1979b) E-chondrites (Crabb, 1980)
and ureilites (Göbel et al., 1977). The 'Q' phase amounts to
between 0.5 - 5% by weight depending on the petrologic type
but contains most of the trapped noble gases. Further mild

treatment of 'Q' with oxidising agents (HNO_3, H_2O_2 or atomic oxygen) results in the opposite effect, namely a mass loss of 10% or less but the removal of 90% or more of Kr and Xe. Most significantly, the isotopic abundance pattern is changed drastically. Normalized to β-shielded ^{130}Xe the light and heavy isotopes are strongly enriched, in extreme cases upto a factor of two or more. A typical CCFXe has a W shape as shown in Fig. 1.5a.

There is some confusion regarding the characterization of 'Q' phase. The Chicago group characterized it to be mainly Fe-Ni and Fe-Cr sulphides and chromite and amorphous carbon (Gros and Anders, 1977). After HNO_3 attack, Q leaves behind a carbonaceous phase part of which has been characterized as Carbynes (Whittaker et al., 1980) the dominant carrier of anomalous Xe, and a little chromite. On the contrary the Berkeley group characterized Q as a pure carbonaceous phase, a portion of which is dissolved on HNO_3 attack (Ott et al., 1979; Frick and Chang, 1978).

Srinivasan and Anders, 1978 have identified yet another more interesting Xe component from the severely etched mineral fraction of the Murchison chondrite. This Xe, released at 1200-1600°C and comprising of 5×10^{-5} of the total Xe, is enriched in the s-isotopes. This is accompanied by Kr, similarly enriched in s-isotopes, though to a lesser extent, and Ne and He highly enriched in the isotopes ^{22}Ne and ^{3}He.
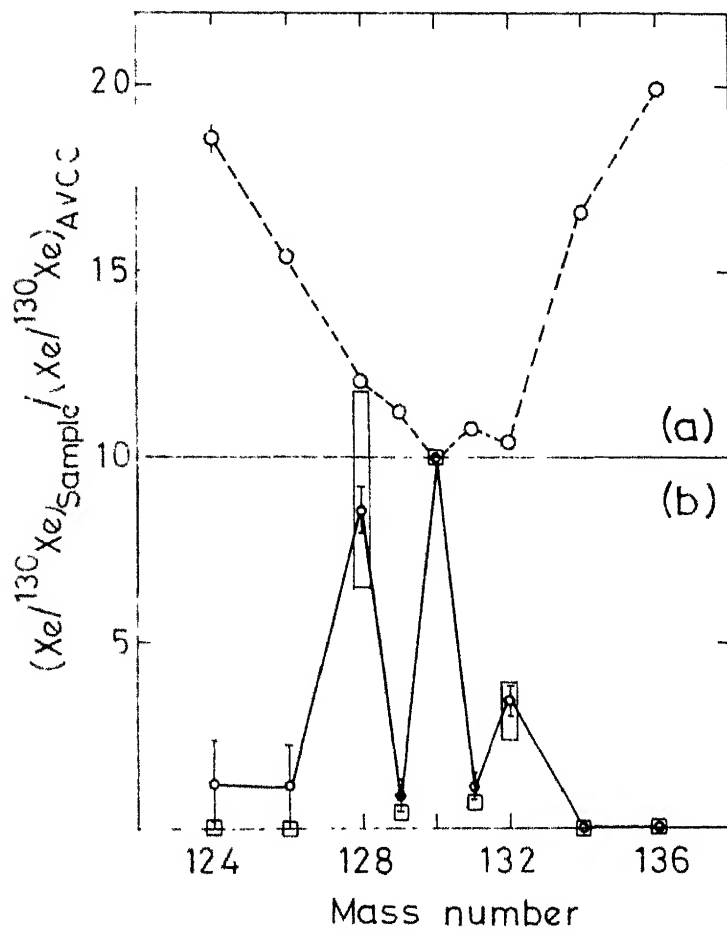
Fig.15(a) CCF Xe (b) Xe-s
Boxes indicate Xe-s calculated for
red-giants (from Begemann,1980)

The s-Xe from Murchison matches well with the s-Xe calculated
by Clayton and Ward, 1978 for the red giants (see Fig. 1.5b).
This component identifies another kind of pre-solar material in
primitive meteorites, dust grains ejected from red giants.
Matsuda and Lewis, 1980 have recently isolated from Muschison
the component 2C10m, having substantial amounts of Ne-E (H and
L) and s-Xe each belonging to a different presolar origin
(Anders, 1981).

An excess ^{132}Xe named 'alien Xenon' has been identified
in the 1650°C fraction of two Allende inclusions (Jordan et al.,
1980). Low energy proton irradiation on REE rich interstellar
grains has been proposed as a possible explanation by the
authors.

Frick, 1977 has identified a krypton component depleted in
light isotopes (78 and 80) and which is linked to excess of
light Xe (124, 126, 128) excess of heavy Xe (131,132,134,136)
and excess of heavy Kr (83,84,86) in Allende meteorite as shown
in Fig. 1.6. The positive Xe and the negative Kr anomaly cer-
tainly does not favour the possibility of mass fractionation
(Frick, 1977).

Possible Explanations : The three components of noble gases
Ne-E (H,L) and s-process Xe and Kr cannot be mimicked by local
processes and must be presolar condensates from highly evolved
stars, that found their way into the early solar system and
survived in the primitive meteorites (Anders, 1981).
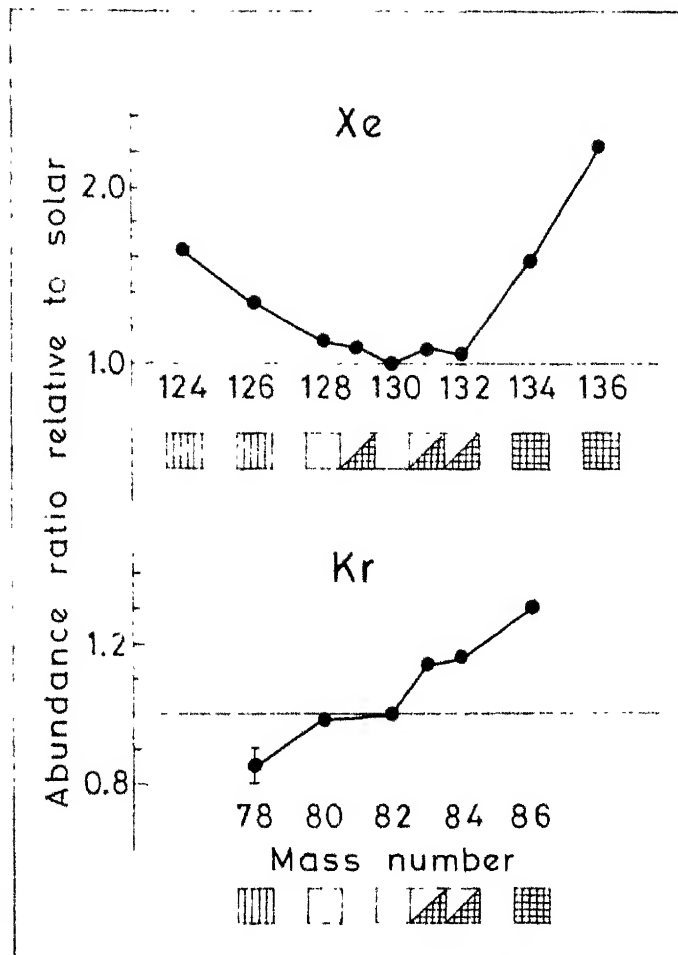
Fig.1.6   Comparison of anomalous Xenon
and anomalous Krypton

▦ p-process , ▢ s-process,
▦ r-process.

(from Begemann ,1980)

The more controversial component is the CCFXe. According to Anders and co-workers the W pattern is due to the superposition of fission Xe and strongly mass fractionated Xenon favouring the light isotopes (Lewis et al., 1975, 1977; Srinivasan et al., 1977; Alaerts et al., 1979a, 1980). According to these authors the calculated Xenon spectrum is different from that of any known fissioning nuclide (Leich et al., 1977; Srinivasan and Flynn, 1980) and hence a superheavy progenitorwas suggested. Various lines of evidence point to an atomic number 113 ± 2 for this SHE (Anders, 1981). A recent experiment to find fission recoils in Allende sulphides, the predicted host minerals of this SHE,has yielded negative results, however (Lewis et al., 1979).

On the other hand, Manuel and co-workers view the correlation of β-shielded light Xe with heavy Xe isotopes as a strong objection to the fission hypothesis and postulate a supernova origin for the anomalous noble gases. Sabu and Manuel, 1980b have noted the correlation of the isotopic ratios and the abundances of noble gases in various meteorites and have come up with a model according to which the solar system itself condensed directly from the chemically and isotopically heterogeneous debris of a single supernova. According to these authors there are two types of planetary noble gases denoted as type-X and type-Y (Manuel and Sabu, 1975, 1977;

Sabu and Manuel 1976a;Frick, 1977; Reynolds et al., 1978).
Type-X gases contain isotopically normal He and Ne but isoto-
pically anomalous Ar, Kr and Xe, and are derived from outer
stellar regions. Type-Y gases contain almost isotopically normal
Ar, Kr and Xe with little or no He or Ne, and are derived from
inner stellar region. Mixing of these nucleosynthetic products
is responsible for the observed elemental and isotopic patterns
of noble gases in meteorites. The correlated Xe and Te anomalies
(Ballard et al., 1979; Oliver et al., 1979) lend strong support
to this view. From the fact that CCFXe is accompanied by a p-
deficient Kr (Frick, 1977) a p-excess Te (Ballard et al., 1979;
Oliver et al., 1979) and a normal Os (Takahashi et al., 1976;
Grossman and Ganapathy, 1976); Heymann, 1979; Heymann and
Dziczkaniec, 1979, 1980a,b; suggested that O- and Ne- shells
and possibly C-shell of a massive star as the astrophysical sites
for the anomalous light Xe component in meteorites. One problem
that still remains unexplained in the supernova model is the
trapping of the highly anomalous Xe in isotopically normal
chromite and carbon in such similar amounts (Alaerts and Lewis,
1978).

Another interesting possibility has been suggested for
CCFXe by Mueller and Schaeffer, 1979. It may be a nuclear
fission process induced by CNO flare particles in the few Mev/
nucleon energy range, on the very heavy target elements like
Au,Hg,Tl,Pb and Bi, during the T-Tauri phase of our Sun.

CHAPTER 2

EXPERIMENTAL

The long lived nuclides ^{14}C and ^3H, produced via $^{14}N(n,p)$ ^{14}C and $^6Li(n,\alpha)$ ^3H reactions respectively, by thermal neutron irradiation, have been used to determine N and Li in a sample. Simultaneous determination of both the elements is possible, by extracting ^{14}C in the form of CO_2 ($BaCO_3$) and ^3H as H_2O, after suitable carriers have been added. A detailed description is given by Shukla et al., (1978). A brief outline of the procedure is described below.

2.1   Packing and Irradiation

2.1.1 <u>Packing</u> : To avoid contamination problems, sample handling, prior to irradiation, is kept to a minimum, possible extent. However, for unavoidable steps, extreme precautions are taken by using clean apparatus and guaranteed reagents. Monitors and separated phases (sieve fractions and minerals) are sealed in capillary quartz tubes, which are finally sealed in a big quartz vial along with the other samples (pieces of meteorites or tektites). Clean interior pieces of meteorites are packed without any further handling. Tektite pieces are cleaned with distilled water, in an ultrasonic cleaner and dried under heat lamp.

Sealing is done under vacuum, by attaching the quartz vials to a manifold, and evacuating the manifold overnight to a vacuum of 40 μm Hg. Some iron meteorite pieces are irradiated in screw capped aluminium containers. A thorough leaching of the surface after irradiation rules out contamination. In case where nitrogen is not the element of interest and lower irradiation dose is sufficient the samples are irradiated in polyethene vials, which are heat sealed under atmospheric pressure.

2.1.2 Irradiation : Irradiations were carried out at the Bhabha Atomic Research Centre, Trombay. Depending on the requirement, samples were irradiated in the CIRUS reactor at a flux of $\sim 10^{13}$ n cm^{-2} sec^{-1} ranging from a week to a month; or in the APSARA reactor at a flux of 10^{12} n cm^{-2} sec^{-1} for 2 days.

2.2 Decomposition and Purification

2.2.1 Decomposition : The irradiated samples were powdered in an agate mortar or stainless steel die, whenever possible (except for iron meteorite pieces). The sample, is mixed with an oxidising flux (1:10 by mass, mixture of fuxed K_2CrO_4 and $PbCrO_4$) about 5 times the sample weight in an alumina fusion boat. 100.0 mg of $CaCO_3$ and 600.0 mg of $Ca(OH)_2$ were added to act as carriers for ^{14}C (recovered in the form of CO_2) and ^3H (recovered as H_2O) respectively, giving, at full recovery, 200.0 mg $BaCO_3$ and 146.0 mg H_2O

respectively. The boat was introduced into a silimanite tube which was slided into a quartz reactor. After evacuation, oxygen (about 15-20 cm Hg) was introduced into the quartz reactor and the reactor was heated to $1050^{\circ}C$ for about 3 hrs, at the end of which, $\overset{*}{C}O_2$ and $\overset{*}{H}_2O$ were recovered respectively, by absorbing in 4N, NaOH (with $BaCl_2$ dissolved in it) as $Ba\overset{*}{C}O_3$ and by collecting $\overset{*}{H}_2O$ in a liquid N_2 cooled trap. All the operations of handling irradiated samples and decomposition were carried out in the 'Hot lab' to avoid contamination in the counting lab which is located on a different floor.

2.2.2 <u>Purification</u> : Radiochemical purification is carried out in a separate lab where the background is normal. Purification for ^{14}C is essential to avoid other volatile activities that might have been trapped in 4N,NaOH.

The $Ba\overset{*}{C}O_3$ precipitate from the 'Hot lab' is decomposed in a closed system, by adding dil.HCl, and the liberated CO_2 is bubbled through 1) 5 percent solution of $KMnO_4$ 2) concentrated CrO_3 in 85 percent H_3PO_4 and 3) $FeSO_4$ in H_2SO_4, by bubbling through it, under reduced pressure, CO_2 free air. The first trap removes SO_2 and Cl, while the second absorbs SO_3 and oxides of N from the gases. The last trap removes any chromic-phosphoric acid solution that might be carried along with the gases (Maxwell, 1968). The purified CO_2 was finally absorbed in 2N,NaOH containing

dissolved $BaCl_2$ (Fig.2.1). NH_4Cl (20 percent) solution was added to quench the excess NaOH in the solution. The $Ba\overset{*}{C}O_3$ precipitate was filtered through a G-4 sintered crucible, washed with hot water, dried in an oven at $120^{o}C$ and finally mounted on copper planchats, by making a slurry with alcohol to get a uniform deposit and then drying it under a heat lamp.

The tritiated water from the 'Hot lab' was first diluted to about 5 ml by adding distilled water, for conveniently handling the sample. This water can be purified by simple distillation. But our experience has shown that this step is not necessary (Shukla, 1977).

2.3 Counting, Corrections and Calculations

2.3.1 Counting of $Ba\overset{*}{C}O_3$: $Ba\overset{*}{C}O_3$ samples were counted on

an end window gas flow counter. The system was model Low Bota manufactured by sharp laboratories, California. The counter is operated in the geiger region having a plateau of 350 volts (1000 to 1350 volts, set at 1150 volts) and a slope of 2 percent/100 volts. Gas mixture of 1.3 percent butane and 98.7 percent Helium was used. The background was frequently counted for long periods and was about 0.5 cpm. Performance of the counter was checked regularly by counting a standard ^{14}C source. Efficiency of the counter for ^{14}C weak β (weightless sample) was about 10 percent. Statistical errors were kept below 3 percent by counting for long periods.
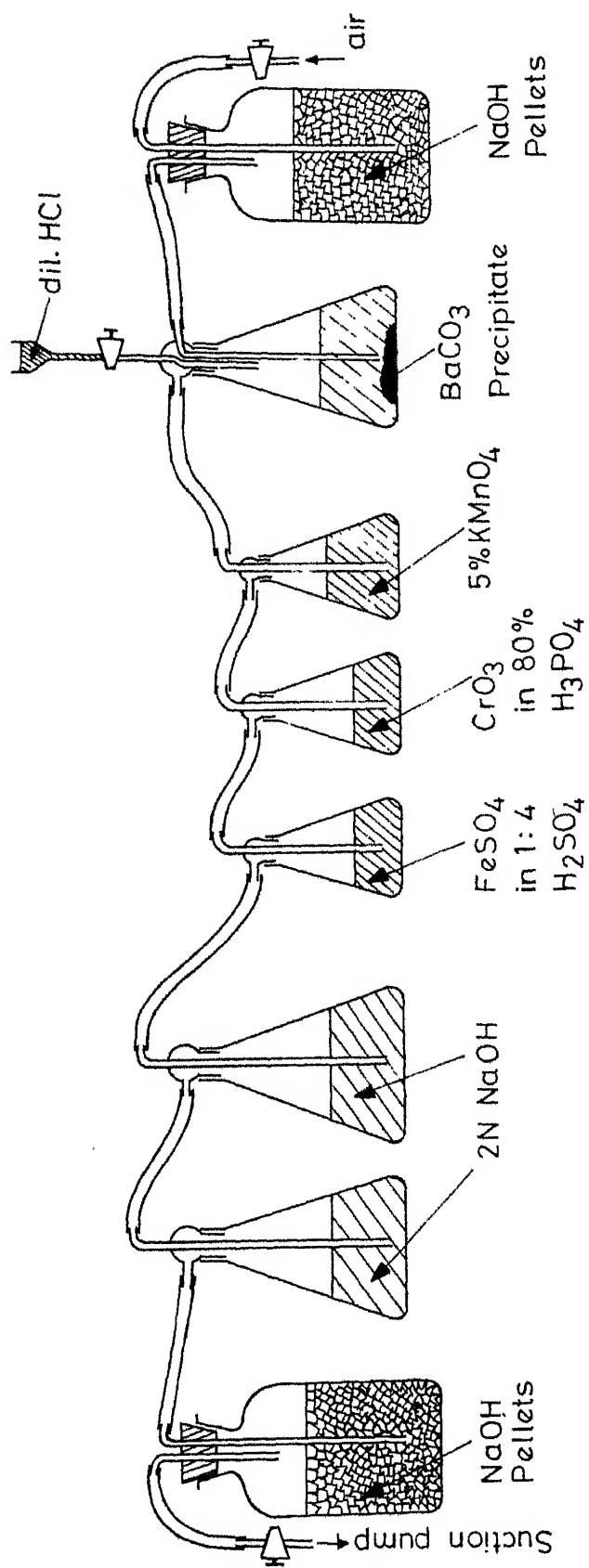
Fig. 2.1 BaCO₃ purification system.

2.3.2 <u>Counting of H$_2$O</u>* : Tritiated water was counted on a
Tri-Carb scintillation spectrometer (Model No. 3003, Packard).
Optimal adjustments were made by using a standard tritium
source. Background was frequently counted and was steady
around 75 cpm. Performance of the counter was monitered by
standard tritium source, regularly.

A sample for counting was prepared by mixing 1 ml of
sample water with 10 ml of scintillation solution, in a low
potassium glass counting vial. The composition of the
scintillation solution was taken from Schram and Lombart (1963)
and is given below.

Naphthalene(Analar)	= 60 gm.
PPO (2,5 -Diphenyloxazole, scintillation grade, Packard)	= 4 gm.
POPOP (1,4-bis-2-(5-phenyloxazolyl)-benzene,scintillation grade,Packard)	= 0.2 gm.
Methanol (Analar)	= 100 ml.
Ethylene Glycol (Analar)	= 20 ml.
Dioxane (Analar) : To make one litre.	

To allow the dissolution of POPOP, the solution was kept
overnight before use. It was stored in a dark place.

2.3.3 <u>Corrections</u> : Self-absorption corrections for the
assay of radiocarbon were made using the standard plot of
thickness vs. activity of the sample with the same specific
activity (Fig. 2.2) prepared earlier by Kothari (1974). In
this plot the activity has been normalized to 10 mg/cm^2, the
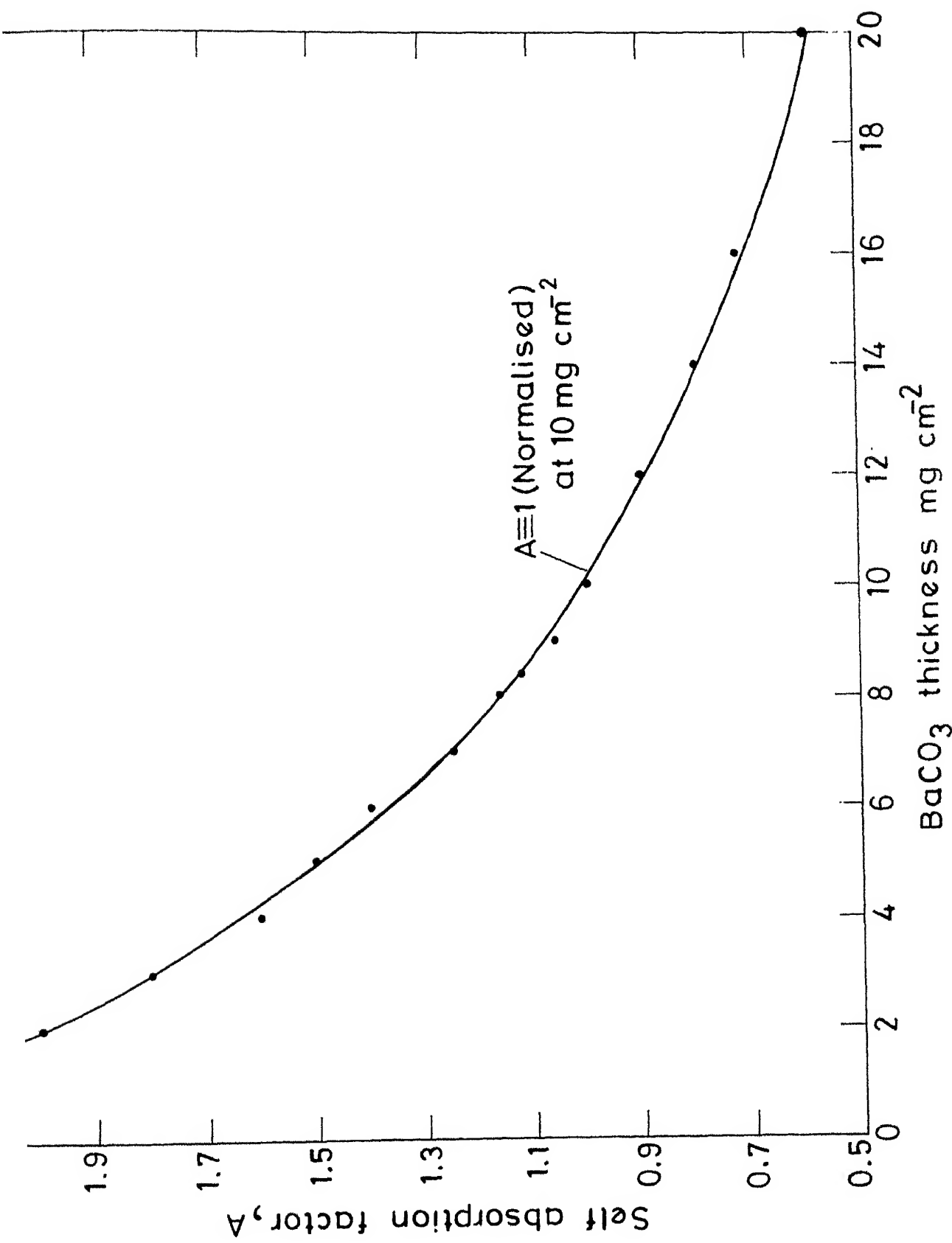
Fig. 2.2   Self absorption (correction) factor, A .

normal thickness of our samples.

2.3.4 <u>Calculations</u> : ·The N or Li content of the sample was determined as follows :

$$\text{N or Li in the sample} = \frac{(^{14}\text{C or }^{3}\text{H activity}) \text{ sam.}}{(^{14}\text{C or }^{3}\text{H activity}) \text{ moni.}} \times (\text{N or Li})\text{moni}$$

NBS-33d with a certified value of 110 ppm N, and BCR-1 with 13 ppm Li (Flanagan, 1973) have been used as monitors for N and Li respectively.

$$^{14}\text{C activity of the sample} = \frac{S(\theta)}{Y} \times \frac{(\text{sample counts per min.})}{(\text{sample mass, gm.})}$$

where $S(\theta)$ is self-absorption correction factor;

$\qquad$ Y = Chemical yield determined by weighing $BaCO_3$

$$^{3}\text{H activity of sample} = \frac{Y \cdot D \cdot (\text{Sample counts per min.})}{(\text{Sample mass, gm.})}$$

where Y = yield factor determined by weighing the $\overset{*}{H}_2O$ collected.

D = Dilution factor = wt. of the water sample after dilution
$\qquad$ with distilled water.

2.4 <u>Errors</u>

From replicate measurements of N and Li on standard samples the uncertainity in our measurements has been assessed to be ± 10% . Isotopic composition of the two elements N, and Li, in the samples and the monitors are assumed to be identical and normal. For iron meteorites the possibility

exists that the isotopic composition of Li is not the same as of the terrestrial materials (Hintenberger et al., 1965; Levsky et al., 1972, 1973; Brick and Allegre, 1980). Hence, for iron meteorites we will report only the ^{6}Li abundances.

2.5 Interference Reactions

2.5.1 Nitrogen measurement : The reaction $^{17}O(n,\alpha)$ ^{14}C interferes with $^{14}N(n,p)$ ^{14}C. By analysing enriched Al_2O_3 (20% ^{17}O enriched) it was found (Shukla, 1977) that the reaction $^{17}O(n,\alpha)$ ^{14}C may contribute about 5 ppm apparent nitrogen for a sample containing 40% oxygen. Such interference is not very serious for samples having high N content (e.g. C1 chondrites) but becomes significant when N content is around 20 ppm (e.g. in tektites and ordinary chondrites). However, our values of N have not been corrected for this interference because its exact value is difficult to assess and because it is any way small. In case of iron meteorites, such interference is absent. It is, therefore, possible to report N contents down to <1 ppm.

2.5.2 Lithium measurements : Besides ^{6}Li(n,α) ^{3}H the reaction ^{3}He(n,p) ^{3}H also contributes towards ^{3}H activity of a sample. The ^{3}H produced from ^{3}He, (assuming only thermal neutrons) is given by

$$^3H(^3He) = 2.04 \times 10^{-4} \frac{[^3He]}{[^6Li]} \times {}^3H(^6Li)$$

where $[^3He]$ = conc. of ^3He expressed in 10^{-8} scc/g units, and $[^6Li]$ = conc. of ^6Li in ppm.

For silicate samples $[^6Li] \simeq 0.1$ and $[^3He] \simeq 5$. Therefore,

$$^3H(^3He) \simeq 0.01 \ ^3H(^6Li)$$

which is negligible. But for a typical iron meteorite $[^3He] = 500$ and $[^6Li] \simeq 0.01$, the contribution from ^3He becomes quite significant. $^3H(^3He) \simeq 10.2 \ ^3H(^6Li)$. This interference will be further discussed, when we report the data on Li in iron meteorites (Chapter 5).

2.6 Comparison of Various Methods for Nitrogen

2.6.1 Merits and demerits of the various methods : There are two difficulties in the determination of trace amounts of nitrogen of geological samples: (i) contamination from the atmospheric nitrogen leading to higher value, and (ii) incomplete extraction in some methods leading to a lower nitrogen content. Of the three classical methods used for nitrogen determination, the carrier gas extraction method is plagued by contamination problems (Gibson and Moore, 1970) while the Kjeldahl method detects only chemically bound nitrogen (Müller et al., 1976). Guiraud and Fardeau, 1977 have concluded by labelling experiments that 'when the total nitrogen is analysed by the Kjeldahl method, the nitrates present in a soil are titrated only in part'. The vacuum

fusion method partially extracts nitrogen leading to incom-
plete recovery (Drew, 1970; Ihida, 1959). Kuznetsov et al.,
(1978) have discussed the 'thermodynamic and kinetic pecu-
liarities' in the determination of nitrogen in refractory
metals by the method of 'reduction melting with pulsed heating'.

On the other hand the activation methods do not distin-
guish between various forms of nitrogen and only 'total
nitrogen' determination is feasible. The γ-activation method
(Berzin et al., 1966) produces the short lived ($t_{\frac{1}{2}} = 10$ min.)
nuclide, ^{13}N via $^{14}N(\gamma,n)\,^{13}N$ which is a positron emitter.
A near reactor facility, with pnumatic tube transfer, is
required for this approach. The thermal neutron activation
produces the long lived ($t_{\frac{1}{2}} = 5720$ y) ^{14}C via $^{14}N(n,p)\,^{14}C$
which can be assayed conveniently.

Atmosphere being a vast reservoir of nitrogen, any
method for the determination of trace amounts of nitrogen
is prone to atmospheric contamination. In the case of
classical methods, contamination poses problems at every
step. In the activation methods, only prior to irradiation.

In the absence of contamination prior to irradiation,
the neutron activation method has the added advantage to
separate various phases and sieving to various size fractions
without any contamination problems, thus enabling very reliable
data on separated phases. It is, therefore, very pertinent
to prove a complete absence of contamination prior to

irradiation in the neutron activation method.

During high temperature mass spectrometric volatalisation studies of unaltered glassy rims of tholeiitic pillow basalts, it was discovered (Delaney et al., 1978) that the amounts of gas released and gas release pattern could be altered by physically altering the grain size. N_2 and CO appeared to be present more in small grain size fraction and the gas release patterns for N_2 and CO from the small grain size fraction were very similar to those from Lunar fines. Ivlifev et al., (1981) also have found that sieving of the sample even in helium atmosphere leads to significant contamination, particularly in the fine grain fractions.

The contamination problem will be most serious, in powder samples due to large surface area for N_2 adsorption. We have designed a set of experiments to check the extent of surface correlated nitrogen in the powdered samples.

2.6.2 <u>Sieving experiment</u> : If there is surface adsorption, it should be proportional to surface area. An increase of nitrogen content with decrease of grain size should be expected. Our results on G-2 (Table 2.1) show the same nitrogen content in < 38 μ and 38-75 μ fractions as in the bulk sample. The slight excess of nitrogen observed in 75-151 μ fraction could be due to mineralogical effects.

Table 2.1 Nitrogen and Lithium in Sieve Fractions of G-2

Grain size μ	Mass mg	N ppm	Li ppm
$<$ 38 μ	23.5	33.6	35.3
38–75 μ	18.5	34.6	35.2
75–151 μ	8.5	55.3	35.8
Bulk	8.5	31.8	35.0

2.6.3 <u>Leaching experiment</u> : If nitrogen is adsorbed on the surface it must be leached out with milder attacking reagents. Aliquots of irradiated BCR-1 sample were leached with 0.1% NaOH, 3M. HNO_3, 1:10 H_2SO_4 and 1% HF for 2 hrs. and after thorough washing, the residues were analysed for nitrogen. The results were shown in Table 2.2 . Except in the case of 1% HF, where a major portion of the sample happens to dissolve, the nitrogen is almost the same in the residues, as in the bulk, showing an absence of surface correlated nitrogen.

2.6.4 <u>Step-wise leaching experiment</u> : To demonstrate that the nitrogen in lunar fines is surface correlated, Kothari (1974) performed a series of step-wise leaching experiments, (Gool and Kothari, 1972) illustrated in the scheme (Fig. 2.3). For the lunar soil 14163, a major fraction of the nitrogen was released in steps 1 to 5, whereas only a minor fraction remained in the final residue (step 6), clearly showing that nitrogen was surface correlated. Adsorbed nitrogen from the atmosphere should also show a similar trend. We carried out similar leaching experiments on powdered samples of BCR-1 and G-2. The results are clearly different from 14163. Most of the nitrogen resides in the final residue (step 6) showing that it is indigenous to the sample and not due to adsorption. In both the cases, the amount of sample dissolved during the 3M, HNO_3 leaching step was very small ($< 2\%$). We have tried step-wise leaching on two

Table 2.2   Nitrogen in Leached Residues of BCR-1

Sample	Leachant	Mass before leaching mg	Mass of recovered residue mg	N (ppm) In the sample	N (ppm) In the residue
6-BCR-1	0.1% NaOH	23.5	20.0	25.2	21.9
6-BCR-1	3M HNO$_3$	11.0	8.0	25.2	23.5
2-BCR-1	1:10 H$_2$SO$_4$	6.5	4.5	26.0	18.2
1-BCR-1	1.0% HF	20.0	3.0	28.5	11.7

Sample (Powdered)

Step 1
CO_2

0.1% NaOH
Leaching

Filtrate

Dry

Dried Mass
Step 2

Residue

Step 3
CO_2

2M.HNO$_3$
Leaching

Step 4
CO_2

Filtrate

Dry

Dried Mass
Step 5

Residue
Dry

Residue
Step 6
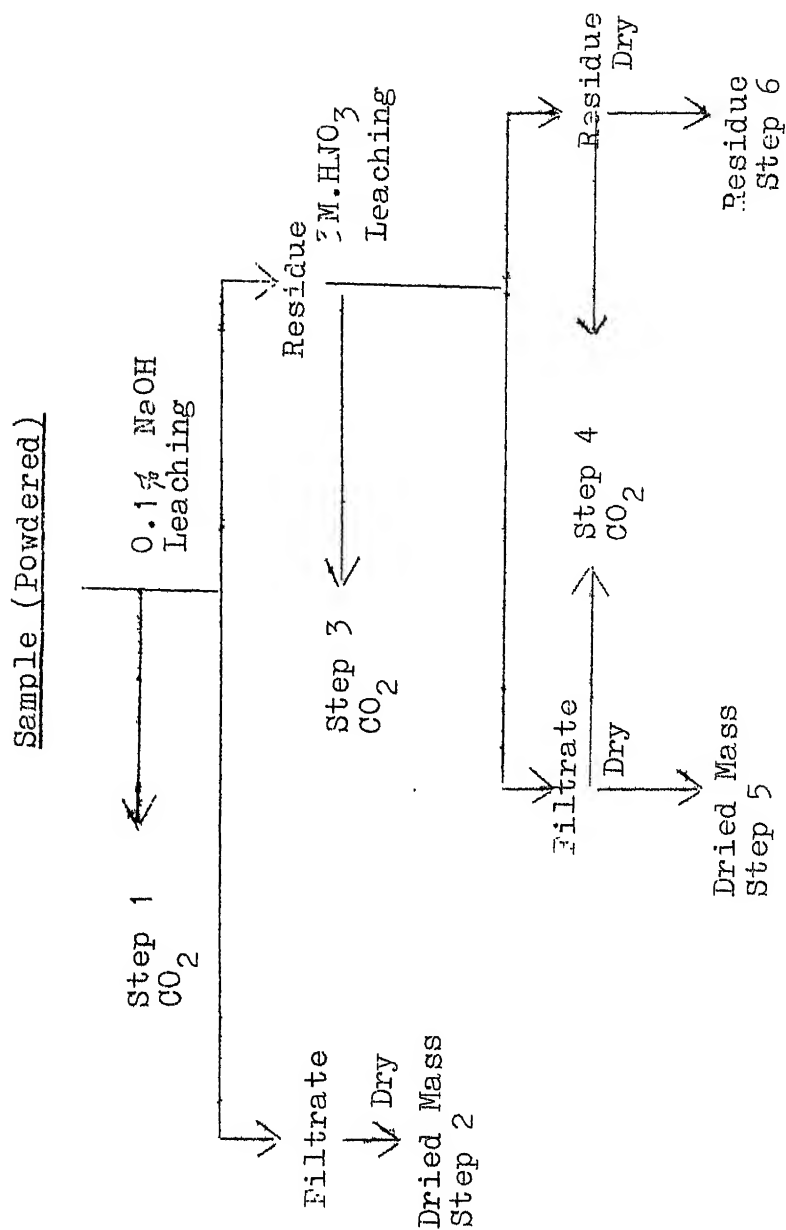
Fig. 2.3   Scheme of the step-wise leaching
experiment

meteorite samples also, where, unfortunately, sample
dissolution during the·3M, HNO$_3$ leaching, presents serious
problems. About 50 percent of the sample dissolves, probably
including a nitrogen bearing phase, giving lower value in
Step 6 (Table 2.3).

The above set of experiments show very conclusively,
that any serious atmospheric contamination is absent in our
work.

2.6.5 <u>Step-wise heating experiment</u> : Recently Norris and
Schaeffer (1980) conducted a step-wise heating experiment on
BCR-1 and found that about 70 percent of nitrogen was
released at 900°C whereas the rest 30 percent was released
at around 500°C. The high temperature fraction, which is
presumably indigenous to the sample,matches with our BCR-1
value for nitrogen. The low temperature fraction could be
according to the authors due to atmospheric contamination
during sample handling.

2.6.6 <u>Problems with the vacuum pyrolysis</u> : Ihida (1959)
has concluded that inspite of the relatively high decomposi-
tion pressure of some nitrides, comparatively large amounts
of nitrogen remains in the melt, even under a dynamic vacuum
of 10^{-4} to 10^{-5} torr. Some of the residual nitrogen was
expelled from the melt upon cooling and some of the 'missing'
nitrogen was recoverable by subsequent analysis of the spent
vacuum fusion-melt. The BISRA (1958) study has shown that

Table 2.3 Results of Step-wise Leaching Experiment (Nitrogen)

Sample	Starting Mass(mg)	N(ppm) in Steps						SUM	N(ppm) expected
		1	2	3	4	5	6		
BCR-1	29.0	0.62	-	2.08 (24.5)*	0	0	18.7 (22.0)	21.4	26.0
G-2	29.5	1.35	2.81	1.59 (29.0)	0	-	23.4 (27.0)	29.25	39.0
Ambapur Nagla	41.0	0.42	2.80	12.4 (38.5)	1.0	1.43	8.15 (22.0)	26.2	31.0
Dhajala	44.5	0.04	1.25	21.2 (43.0)	1.13	3.0	10.0 (22.0)	36.8	35.7
Amb.Nagla <38μ,Mag.	1.83	-	-	13.9	-	-	654.0	-	758.0
14163**	77.0	1.3	4.0	22.0	-	6.0	15.0	48.3	80.0

*   Mass of the residue at this stage (Refer Fig. 2.3) in mg.

**   From Kothari, 1974.

the last traces of nitrogen become progressively more and more difficult to extract, in the vacuum fusion method, particularly in the presence of strong nitride forming elements (Al, Si, Zr and Ti) in the melt. Also Moore (1976, private communication) assesses that 'the N is held by strong covalent bonds such as Si-N-Si in the structure of silicates and is not removed by incomplete acid attack in Kjeldahl analysis, or by vacuum fusion in isotope analysis'.

A comparison of nitrogen values by the vacuum pyrolysis method, with those determined by other methods (Table 2 of Becker and Clayton, 1975) in the lunar samples brings out the following facts : 1) A reasonably good agreement exists in the case of lunar soils. This is due to the fact that most of the nitrogen in lunar soils is surface implanted and easily extractable by the vacuum pyrolysis method. 2) In the case of breccias and rocks the agreement is very bad, presumably due to the incomplete recovery of the more tightly bound indigenous nitrogen in these samples. 3) Also the preheating of the sample upto $200^{\circ}C$ to degas the atmospheric adsorbents might be extracting some amount of easily recoverable nitrogen, along with helium which is shown to be partially lost during the preheating step (Becker and Clayton, 1975).

Clayton contends that the method followed by his group ensures complete extraction of nitrogen from the samples as

evidenced by the recovery of the most tightly bound spallo-
genic nitrogen upon melting the sample. This conclusion has
been arrived by computing spallation ages from the highest
temperature fraction of nitrogen (which they attribute
totally to spallogenic component) and its $\delta^{15}N$ value. This
does not ensure complete recovery of nitrogen as argued
below.

The equation $t_{spal} = \delta^{15}N \cdot (ppmN)$ where both $\delta^{15}N$ and
(ppmN) correspond to the highest temperature fraction
(Becker et al., 1976) can give a fortutiously agreeable
spallation age, even if both $\delta^{15}N$ and (ppmN) are in large
error, as long as the product matches. Contamination from
low temperature fraction to the high temperature fraction
of nitrogen can increase (ppmN); but $\delta^{15}N$ decreases because
the low temperature fraction is lighter isotopically. Still
the product $\delta^{15}N \cdot (ppmN)$ can give an age which fortutiously
matches with the spallogenic age in some cases (Becker
and Clayton, 1976). Also the lunar regolith is known to
have 1-1.5% of meteoritic component of C1 type (Anders et al.,
1973) which can contribute 10-15 ppm N to the lunar soil. The
meteoritic nitrogen has a complex isotopic pattern as shown
by step-wise heating experiments (Frick and Pepin, 1980).
This mixes up with the isotopic pattern of the lunar soil and
the resultant isotopic pattern cannot be taken too seriously
as an index of any process. In fact, the best candidate for

looking at spallogenic nitrogen will be the lunar rock sample, but not the soil or breccia which have undergone lot of communition and trapped solar wind nitrogen and meteoritic nitrogen during their exposure epochs.

2.6.7 <u>Comparison of data</u> : For the purpose of inter-calibration of standards and to understand the discrepancies in the three methods (Kjeldahl, RNAA and inert gas carrier methods) we have analysed standards used by the Arizona group (inert gas carrier pyrolysis) and the Heidelberg group (Kjeldahl). In Table 2.4, our values are compared with the other groups. There is a serious disagreement between Müller's values for G-2 and W-1 and our values. This may be due to the preferential extraction of certain chemical forms of nitrogen only, in the Kjeldahl method (Müller et al., 1976). Our BCR-1 value agrees well with that of Moore. But our DTS-1 value is a factor of 2 lower.

In Table 2.5 nitrogen values for many geological standards, analysed in our laboratory are compared with literature values. Within the limitations of the other techniques the agreement is reasonable, except for Clayton's values which are too low. This must be due to incomplete extraction, and one plausible reason for the incomplete extraction by the vacuum pyrolysis method for geological standards in particular, may be due to the form of nitrogen in these samples. If nitrogen is present in the form of refractory nitrides, it will be difficult to extract (Ihida, 1959; BISRA, 1958).

Table 2.4   Inter-laboratory Comparison   of N data on
             Standards

Sample (source)	N(ppm) Replicate	Mean	N(ppm) Moore/Müller
BCR-1 (Moore)	26.6,30.4,26.7, 32.0,21.9,25.5	27.2	30.0
DTS-1 (Moore)	14.4,11.2	12.8	27.0
BVHO-1 (Moore)	28.5,28.7	28.6	
G-2 (Müller)	36.4,35.5,44.0, 38.5,31.8	37.2	8 ± 2
W-1 (Müller)	34.9,36.7,32.6, 38.2	35.6	14 ± 0.6

Table 2.5 Comparison of N data for Terrestrial
          Standards

Sample	N(ppm) Replicate	N(ppm) mean	N(ppm) literature
BCR-1	31.3,25.3,45.8,36.2,21.0,29.4, 26.6,30.4,29.8,32.1,26.7,32.0, 26.7,25.4,21.9,25.5,21.2,24.1, 32.2,32.2,41.2,48.3,38.8,26.4, 47.9,43.6,43.4 (58.0,68.0,57.0,55.0,57.0,55.0)* (51.0,63.0,56.0,56.0,52.0,42.0, 50.0,30.0,39.0,37.0,45.0,32.0, 31.0,36.0,29.0,33.0,36.0)**	38.5	30^1, 63^4 77^3, 1.3^2
G-2	36.4,35.5,44.0,38.5,31.8 (36.0,41.0,33.0)**	37.0	56^1,8 ± 2^5 2.3^2
DTS-1	14.4,11.2,18.0*	14.5	27^1
W-1	32.6,38.2,34.9,36.7	35.6	52^1,14 ± 0.6^5
BVHO-1	28.5,28.7	28.6	
AGV-1**	38.0,39.0	39.0	41^1
GSP-1**	31.0,35.0,39.0	32.0	48^1
PCC-1*	47.0	47.0	43^1

Table 2.5 (contd...)

Sample	N(ppm) Replicate	N(ppm) mean	N(ppm) literature
NIM-P	42.6,41.6	42.1	-
NIM-S	41.3,41.9	41.6	-
NIM-L	51.9,48.7	50.3	-
NIM-N	49.2,48.6	48.9	-
NIM-D	33.7,32.6	33.1	-

1. Gibson and Moore, 1970; 2. Becker and Clayton, 1977b;
3. Norris and Schaeffer, 1980 (Preprint);
4. Petrowski, 1974 (Private Commu. to BK Kothari);
5. Müller, 1976
*   Kothari, 1974 (Thesis); ** Shukla, 1977 (Thesis).

2.7 Comparison of Various Methods for Lithium

2.7.1 Merits and demerits of various methods :

Though a number of methods are available for the determination of trace amounts of Lithium (Nichiporuk and Moore, 1970 and references therein) neutron activation methods offer decisive advantages. The secondary product ^{18}F produced via the reactions $^{6}Li(n,\alpha)^{3}H \longrightarrow ^{16}O(^{3}H,n)^{18}F$ (Quijano-Rico and Wänke, 1969) has been used for the determination of Li, but this procedure requires a near irradiation facility due to the short half life of $^{18}F(t_{\frac{1}{2}} = 1.8$ hr). We have used ^{3}H produced via $^{6}Li(n,\alpha)^{3}H$, which has 13 years half life, for Li determination. Due to the long half life of ^{3}H, it can be very conveniently measured. Zverev et al., (1972) have also employed the same method for Li determination.

The most advantageous factor in neutron activation method is the very small amount of sample required. For a chondritic meteorite where Li is about 1.5 ppm, less than 1 mg. amount will suffice in our method, whereas in atomic absorption method a minimum of 250 mg. is required for a reliable measurement (Nichiporuk and Moore, 1970). The small sample requirement allows us to study Li distribution in separated phases. Moreover, the phase separations, involving usage of reagents can be carried out on irradiated material, without fear of contamination.

2.7.2 <u>Difficulties with activation method</u> : There are two difficulties with our method. 1) Escape of ^{3}H from the grains and 2) interference from ^{3}He(n,p)^{3}H reaction. These problems will be of relevance in very specific cases and will be discussed in Chapter 5, where Li in iron meteorites is presented.

2.7.3 <u>Comparison of data with literature values</u> : Table 2.6 shows our results of Li on terrestrial standards like W-1, G-2 etc. with those by other methods. An excellent agreement can be noticed. In case of stone meteorites also the agreement is excellent (for data refer Chapter 4).

2.8 <u>Instrumental Neutron Activation Analysis</u>

In our programme of N,Li determination by RNAA, for a number of samples, we recorded their γ-ray spectra on a pure Ge detector, prior to decomposition. Because of the long irradiations used (30 days) at $\sim 10^{13}$ n cm^{-2} sec^{-1}, for a good build up of ^{3}H and ^{14}C activities in the sample and subsequent cooling time of about 2 months to a few years, it was possible to get the concentrations of only long lived nuclides. Added to this, the high ^{60}Co activity in meteorite samples masked the other activities. But we have been successful in the case of tektite and glass samples in measuring about 10 elements by INAA, after one weeks irradiation, followed by a 2 months cooling time.

Table 2.6   Comparison   of Lithium data for Terrestrial
            Standards

Sample	Li(ppm) Replicate	Li(ppm) Mean	Li(ppm) Literature
BCR-1	≡13	≡13	
G-2	30.8,31.2,23.6, 31.2,35.0	30.4	34.8[1],35[2],40[3]
W-1	13.9,13.7,13.4, 12.6	13.4	14.5[1]
BVHO-1	5.3, 5.8	5.6	-
DTS-1	2.4, 2.0	2.2	2[1], 3[2]
NIM-P	4.3, 4.5	4.4	4[1]
NIM-L	32.0,30.3	31.1	70[1]
NIM-S	1.7, 1.5	1.6	3[1]
NIM-N	6.2, 6.0	6.1	6[1]
NIM-D	4.1, 4.3	4.2	5[1]

1.   Flanagan, 1973;   2. Sengupta, 1968; 3.   Taylor et al.,1970.

2.8.1 <u>Sample preparation</u> : Samples are mounted in perspex sample holders as shown in Fig. 2.4a and covered with a mylar film, so that there is no spilling of the active sample. These sample holders can be held in a fixed and reproducible geometry in the perspex sample mount (Fig.2.4b) which snugly slips on to the detector. This arrangement ensures the same geometry for all the samples.

2.8.2 <u>Spectrum recording</u> : Spectra are recorded on a Canberra pure Ge detector system (Model 7229P). It is a closed end coaxial detector with the following characteristics: Length = 28 mm; Active area facing window = 12.5 cm^2; Distance from window = 5 mm; Thickness of n-layer = 0.5 mm. At the operating voltage of + 2000 volts, it gives a resolution of 3 Kev (FWHM) for 1332 Kev peak of ^{60}Co. It is coupled to a 1024 channel analyser (series 30 of Canberra). The data are printed out on a Teletype printer by interfacing it with the M.C.A. The block diagram of the counting set-up is shown in Fig. 2.5. A Hg shielding is used to reduce the background.

2.8.3 <u>Energy calibration</u> : The energy scale is calibrated so that a maximum energy of 2 Mev can be recorded within 1-1024 channels. To encompass all the regions,the following calibration standards are used. ^{57}Co (122 and 136 Kev) ^{137}Cs (662 Kev) ^{22}Na(511 and 1274 Kev) and ^{60}Co (1173 and 1332 Kev). A very good linear energy calibration is
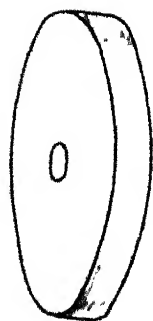
(a)
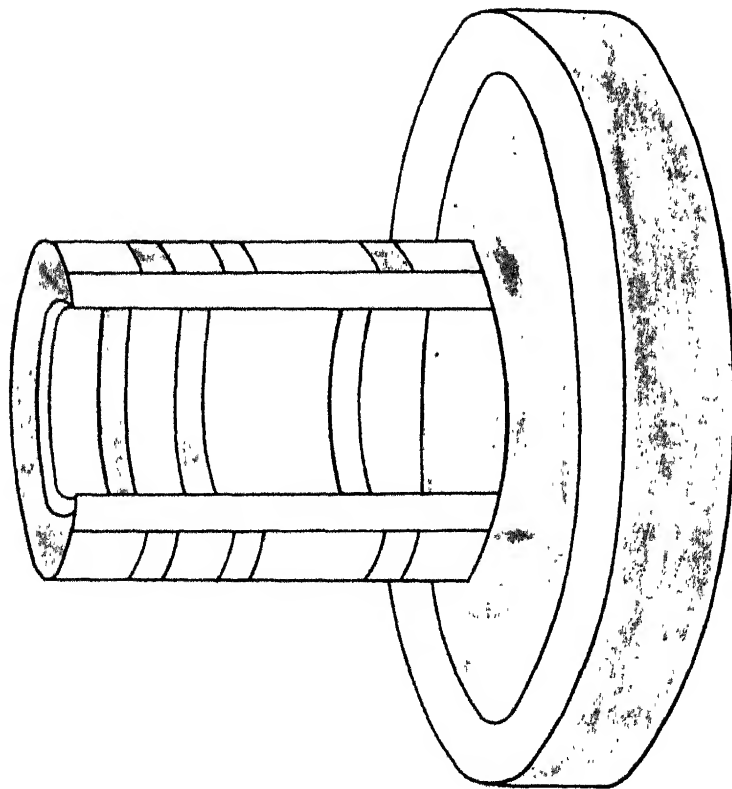
(b)

Fig. 2.4 Perspex sample holder (a) and mount (b).
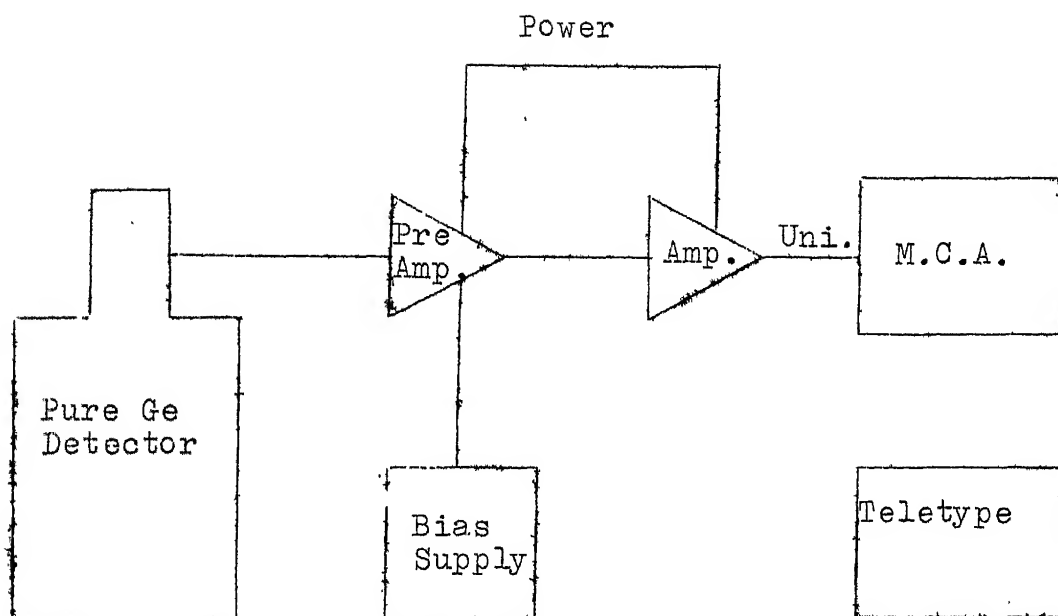
Fig. 2.5 Block diagram for the γ-counting set-up

obtained as shown in Fig. 2.6. Calibration is checked periodically to ensure stability of the amplifier gain.

2.8.4 Data processing : Depending upon the level of sophistication and the accuracy required there are a number of computer programmes available (Baedecker, 1976; Philips and Marlow, 1976) for the data reduction. Due to lack of automatic data transfer facility to the computer and the tediousness involved in manually feeding the data to the computer, which takes much more time than taken for data reduction using a hand calculator, made us opt for the latter.

Peaks are identified by visual inspection of the printout. Correct identification of the nuclide corresponding to the energy peak and subsequent estimation of the element are done under the following guidelines.

a) We have used BCR-1 as the geochemical standard. All determinations are therefore with respect to this standard. The data for BCR-1 are taken from Flanagan (1973). Hence, only peaks which are present both in BCR-1 and the sample are considered. The spectra of BCR-1 and a tektite are shown in Fig. 2.7 and Fig. 2.8 respectively.

b) Only peaks, where peak area > 3 (Base area)$^{\frac{1}{2}}$ are considered to be of statistical significance (Yule, 1966).
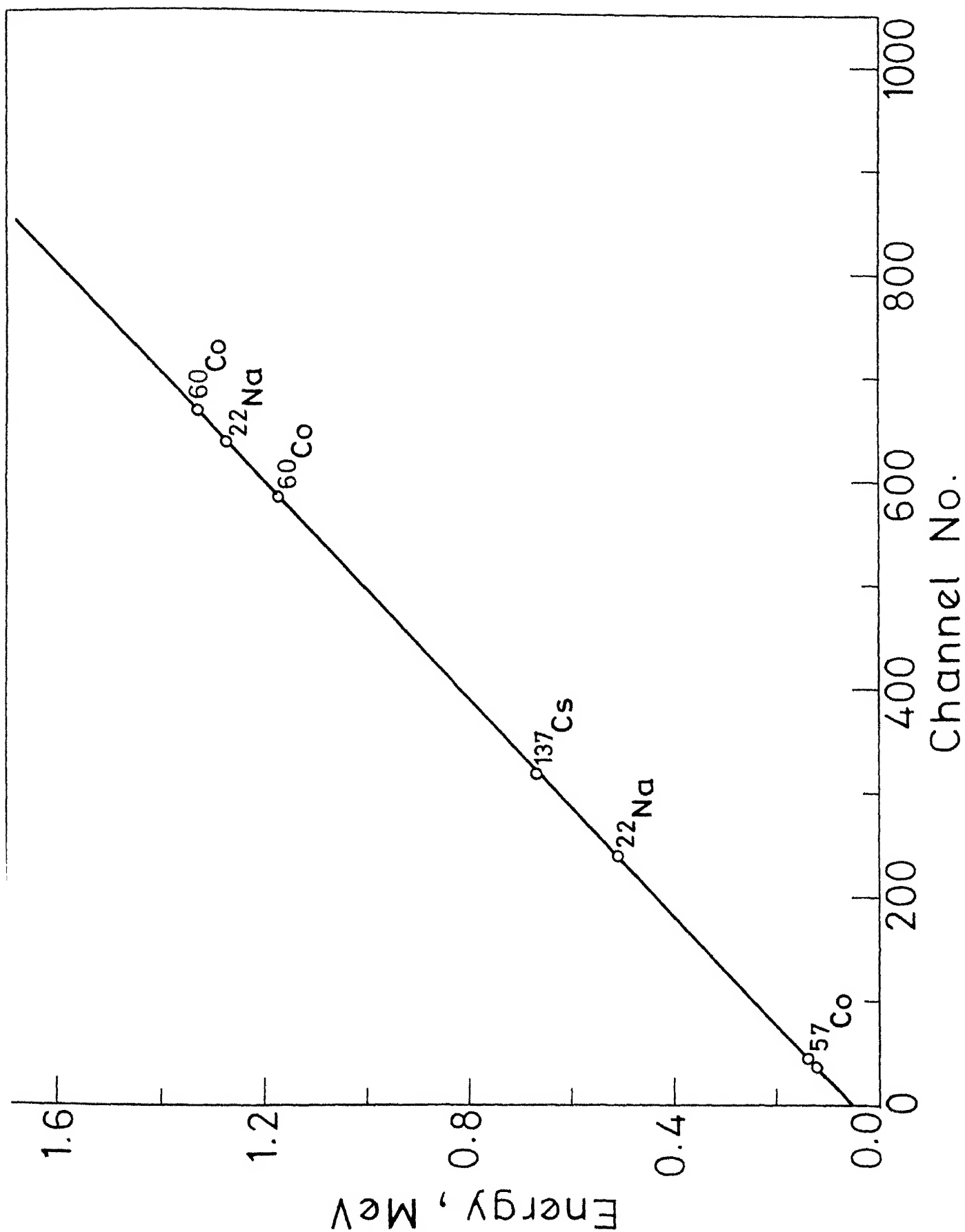
Fig. 2.6   Energy calibration curve.
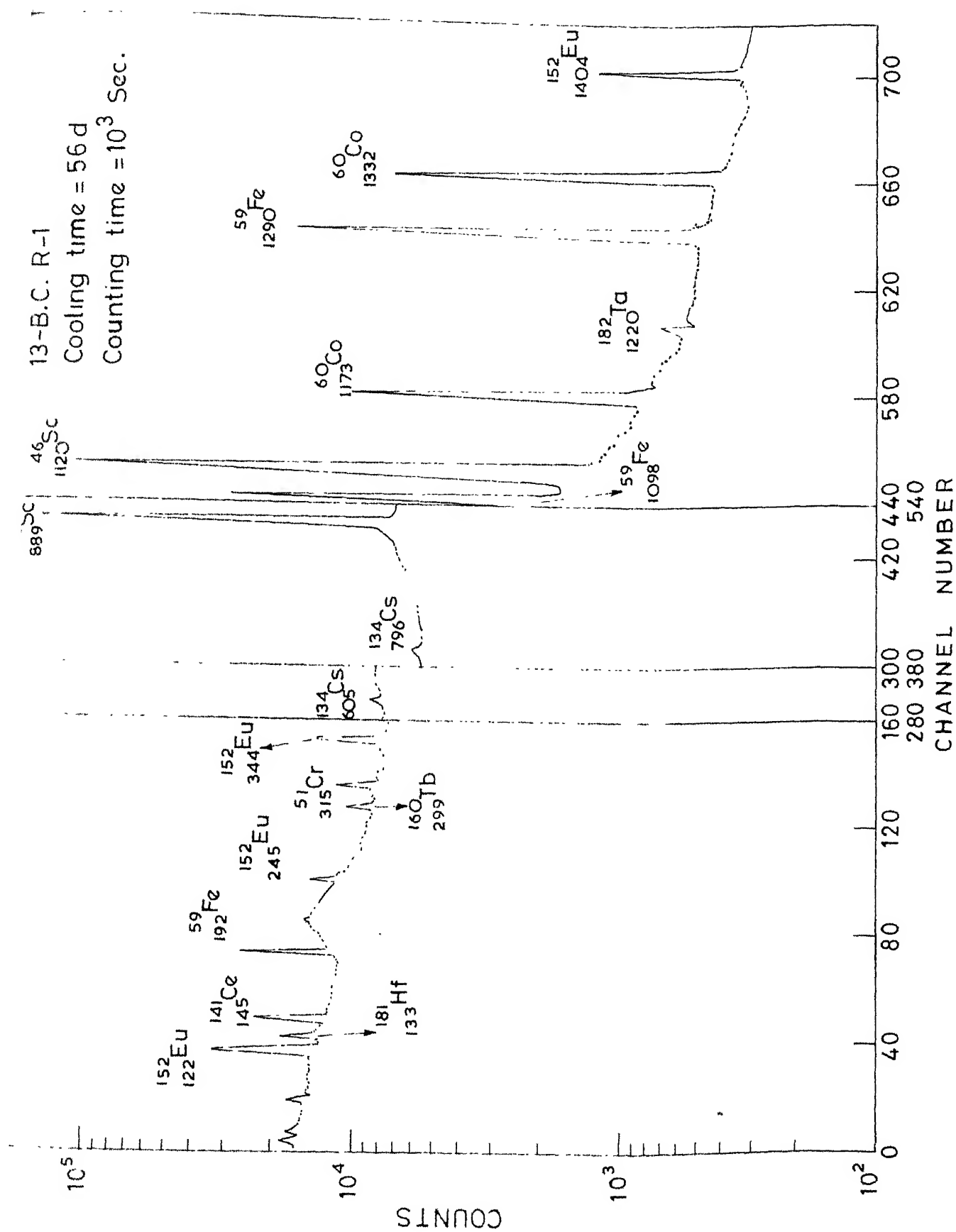
Fig.2.7 Y-Spectrum of 13-B.C. R-1.
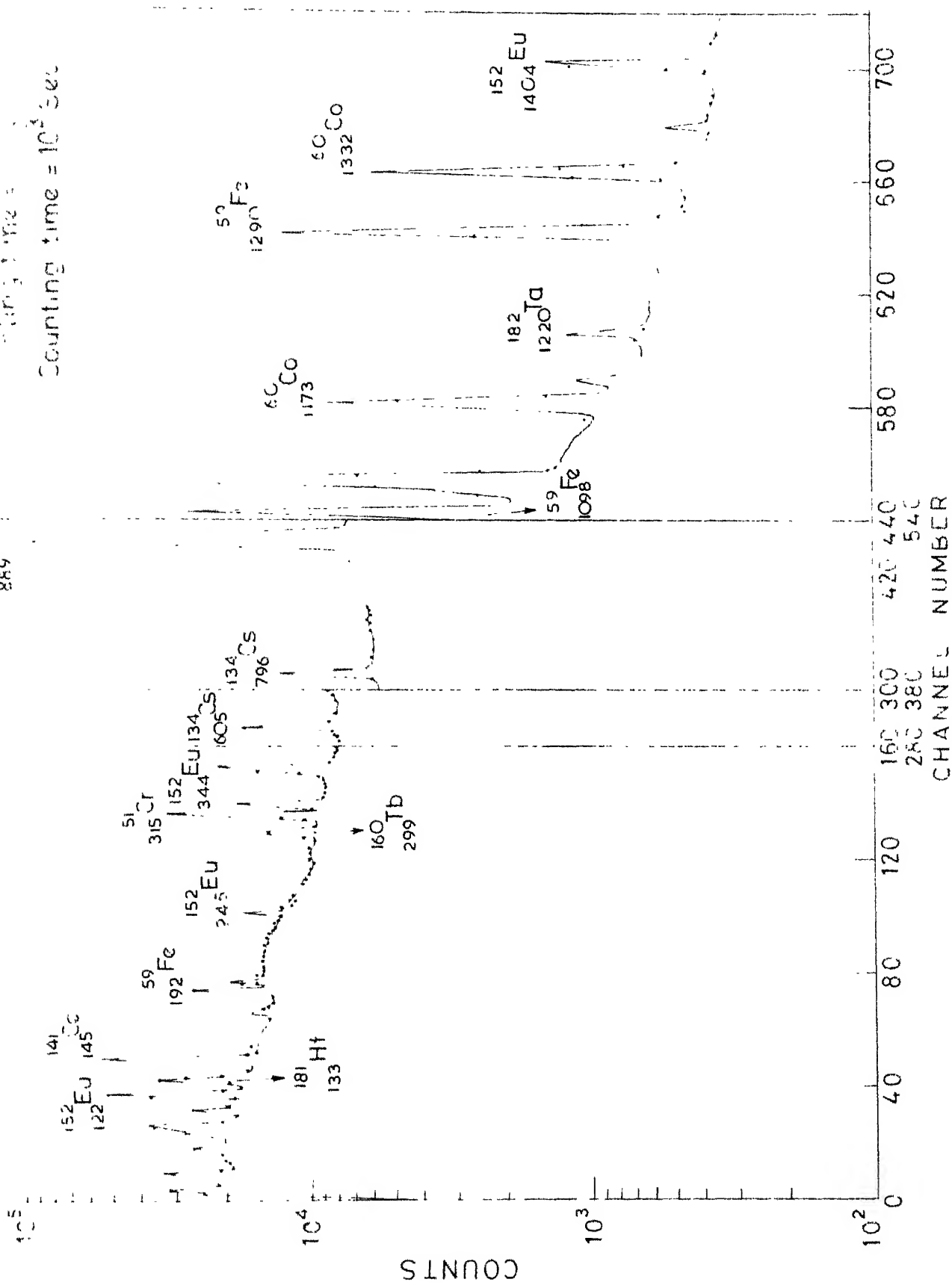
Fig. 2.8   γ-Spectrum of 13-Muong Nong Type Tektite.

c) A background spectrum is recorded for the same time as the sample and standard, to ensure neat background in the region of interest.

d) For correct assignment of the peaks to a particular nuclide all peaks corresponding to the main γ-energies of the nuclide, must be present in the spectrum. We calculated the relative intensities of the peaks with respect to ^{60}Co peaks (which can be unambiguously identified as it is one of the calibration standards) assuming a peak to be due to a particular nuclide; using the following equation :

$$D = \frac{ap\sigma nN}{A} (1-e^{-\lambda t_1})e^{-\lambda t_2}$$

where

D = activity at the time of counting in disintegrations per unit time

a = abundance of element X

p = fractional abundance of the parent nuclide (100 percent = 1)

σ = thermal neutron cross-section

n = neutron fluence

A = atomic weight of target nuclide

N = Avogadro number

t_1 = duration of irradiation

t_2 = cooling time

λ = decay constant.

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n = neutron fluence

A = atomic weight of target nuclide

N = Avogadro number

t_1 = duration of irradiation

t_2 = cooling time

λ = decay constant.

In the calculations n,N and the factor 10^{-24} for σ are omitted as they are common to all. The results are given in Table 2.7, where the relative intensities of the calculated peaks are compared with the actual values from the spectra. A reasonable agreement is taken as a sign for the genuineness of the assignment.

e) When a nuclide has more than one peak, a good match between values calculated from all the peaks has been obtained, which further proves the correctness of the assignments.

f) Peak areas are calculated using the methods of Covell (1959) and Yule (1966) as illustrated below.

The highest counts point is considered to be the centre of the peak. To the right and left of the centre, points R and L are chosen as the base points. The number of channels included in the peak will be (R-L-1) [from L+1 to R-1]. Then if D_i is the counts in channel i.

$$\text{Base area} = \frac{D_L + D_R}{2} (R-L-1)$$

$$\text{Peak area} = \sum_{i=L+1}^{R-1} D_i - \text{Base area}$$

For a given peak, the same R and L are chosen in all the samples and the standard. The standard deviation of the peak area is given by

$$\sigma = (\text{Peak area} + \text{Base area})^{\frac{1}{2}} = \left\{ \sum_{i=L+1}^{R-1} D_i \right\}^{\frac{1}{2}}$$

Table 2.7 Comparison of Calculated and Experimental Relative Photopeak
Intensities

Isotope	Abundance of parent P(percent)	Cross-section σ (Barn)	Half life	BCR-1 abundance a(ppm)	Activity after 56 days calculated		In 13-BCR-1
					Absolute D	Relative to ^{60}Co	
^{45}Sc	100	25	83.82d	33	0.649	11.16	11.56
^{51}Cr	4.345	16	27.8d	17.6	9.51×10^{-3}	0.1637	0.287
^{59}Fe	0.33	1.2	45.0d	6.65%	0.1926	3.31	2.813
^{60}Co	100	37	5.26y	38	5.812×10^{-2}	1	1
^{134}Cs	100	29.9	2.06y	0.95	1.298×10^{-3}	2.233×10^{-2}	7.617×10^{-2}
^{141}Ce	88.48	0.56	32.53d	53.9	7.96×10^{-3}	1.37×10^{-1}	1.36
^{152}Eu	47.82	8304	14.0y	1.94	4.78×10^{-2}	0.822	0.679
^{154}Eu	52.18	480	7.8y	1.94	5.314×10^{-3}	0.0914	0.0901
^{160}Tb	100	27	72.4d	1.0	6.4×10^{-3}	0.1101	0.2833
^{181}Hf	35.24	12.2	42.4d	4.7	4.83×10^{-3}	0.0831	0.588
^{182}Ta	99.988	22.01	115d	0.91	3.24×10^{-3}	5.58×10^{-2}	1.53×10^{-2}

The abundance of element $(X)_{samp.}$ in the sample is simply given by

$$(X)_{samp.} = \frac{(\text{Peak area corresponding to X})_{samp.}}{(\text{Peak area corresponding to X})_{std.}} \, (X)_{std.}$$

The error in the calculation of (X) is given by the standard deviation

$$\sigma_X = \{ (\sigma_X)^2_{std.} + (\sigma_X)^2_{samp.} \}^{\frac{1}{2}}$$

2.9 Osmium Isotopic Ratio by RNAA

The two isotopes of Osmium ^{184}Os and ^{190}Os on thermal neutron irradiation give ^{185}Os and ^{191}Os respectively with half lives of 94 days and 14.6 days. A weeks irradiation at a flux of $\backsim 10^{13}$ n cm^{-2} sec^{-1} and about a months cooling for the decay of short lived activities to reduce the radiation hazard, are very convenient to follow-up both the activities, after radiochemically separating Osmium, and determine the isotope ratio (See Table 2.8 for the nuclear parameters).

2.9.1 <u>Brief outline of the procedure</u> : Osmium can be very easily separated from solution, by distilling it as OsO_4 (Herr et al., 1960; Laul et al., 1970) using HNO_3 or H_2O_2 as the oxidants. The radiochemical purity achieved is very good. The ion-exchange method employed by Morgan (1965) is also a good method, but involves more than one step. After separation, the distillate in a screw capped polyvial, can

Table 2.8 Nuclear Parameters of ^{184}Os and ^{190}Os

Isotope	Abundance (%)	Isotope produced	Cross-section σ Barn	Half-life $t_{\frac{1}{2}}$ days	Main energies Kev.
^{184}Os	0.018	^{185}Os	3000	94	70,646
^{190}Os	26.4	^{191}Os	13	14.6	129

be counted on a pure Ge detector, coupled to a 1024 channel MCA. The ratio of the peak areas (129 Kev peak for ^{191}Os and 646 Kev peak for ^{185}Os) gives a measure of ^{191}Os/^{185}Os of the sample. Using a standard sample with known ratio, it will be possible to determine the ratio for the sample. The detailed procedure involves three steps as described below.

2.9.2 <u>Sample dissolution</u> : Alkali fusion (Morgan, 1965) and acid digestion (Herr et al., 1960; Laul et al., 1970) have been used for the sample dissolution in general. The alkali fusion may cause some loss of Os activity due to volatile oxide formation (Morgan, 1965). Herr's procedure works only for iron meteorites, whereas Laul's HF + H_2SO_4 mixture did not dissolve our iron meteorite residues. We have adopted the acid (HF, HNO_3 and $HClO_4$) dissolution technique used by Belt Jr. (1967). This technique has been successfully used by Nichiporuk and Moore (1970) for the determination of Li in meteorites. The actual dissolution of the sample is carried out in the following sequence.

1) To about 0.5 gm of powdered sample in a teflon beaker 2 ml of distilled water, 20 ml of 48 percent HF and 10 ml of HNO_3 are added. The solution is allowed to stand for 2 hrs.

2) 2 ml of 70 percent $HClO_4$ is added to the above solution and fumed till no white fumes came-off.

3) The inside of the beaker is washed with 1 ml water and the contents are dried.

4) The temperature is slightly raised and 5 ml HCl is added and boiled, till everything goes into solution. 10 ml water is added slowly, while boiling and the contents are dried.

5) The solution is finally made 5-10 ml. in 6 N,HCl.

To prevent the possibility of Os getting oxidized (by HNO_3) to OsO_4 and thereby escape, the Os carrier is added only in the distillation flask. Depending on the sample amount the reagents used for dissolution are proportionally reduced/or increased.

2.9.3 <u>Preparation of Os carrier</u> : A 0.5 gm. ampule of OsO_4 is broken and completely transferred to a 100 ml Erelenmeyer flask having 20 ml of conc.HCl. It is properly stoppered (without greeze) and left overnight. The initially formed $(OsO_2Cl_4)^{2-}$ finally gets reduced to $(OsCl_6)^{2-}$ (Griffith, 1967). The contents are transferred to a 100 ml volumetric flask. The Erelenmeyer flask is rinsed with 5 ml conc.HCl and subsequently with water and the washings transferred to the volumetric flask which is finally made up with distilled water. This gives $(OsCl_6)^{2-}$ in 3M,HCl. One ml of this solution will have 3.75 mg Os.

2.9.4 <u>Distillation</u> : The sample solution in 6 N,HCl is transferred to a 100 ml R.B. flask with B-19 joint, containing few broken glass pieces (to prevent bumping during distillation).

Then 2 ml of Os carrier is added to the flask and the whole
flask is kept in an ice bath. After sufficient cooling
10 ml of H_2SO_4 is added slowly. After further cooling
10 ml of 30% H_2O_2 is added very slowly taking care to prevent
spilling of the contents of the flask. Then the flask is
fitted with a standard water cooled condenser with a 100 ml
R.B. flask, kept in ice bath at the other end, as receiver.
In the receiver flask 5 ml 6N,HCl with thiourea (5 percent)
dissolved in it, is kept as absorber for OsO_4. Using a
heating mantle, the distillation is carried out at $110^{\circ}C$
for about 1 hr when almost complete distillation is achieved.
At the receiving end OsO_4 forms a thiourea complex which
is   violet in colour (Sauerbrunn and Sandell, 1953). In
the distillation set up no greeze is used, to prevent redu-
ction of OsO_4 to OsO_2 (Lundell et al., 1959). The chemical
yield can be determined by measuring the absorbance of the
violet thiourea complex at λ = 480 mµ with a spectro-
photometer (Herr et al., 1960). But we have not attempted
to determine the yield, as we were only interested in the
ratio of activities but not in absolute amount of Osmium in
the sample.

2.9.5 <u>Activity measurement</u> : The violet distillate is
transferred into a 25 ml screw capped polyvial. All samples
are made-up to the same volume (�ᴀ 10 ml) to prevent
absorption effects (Gijbels, 1967). Counting is done on a
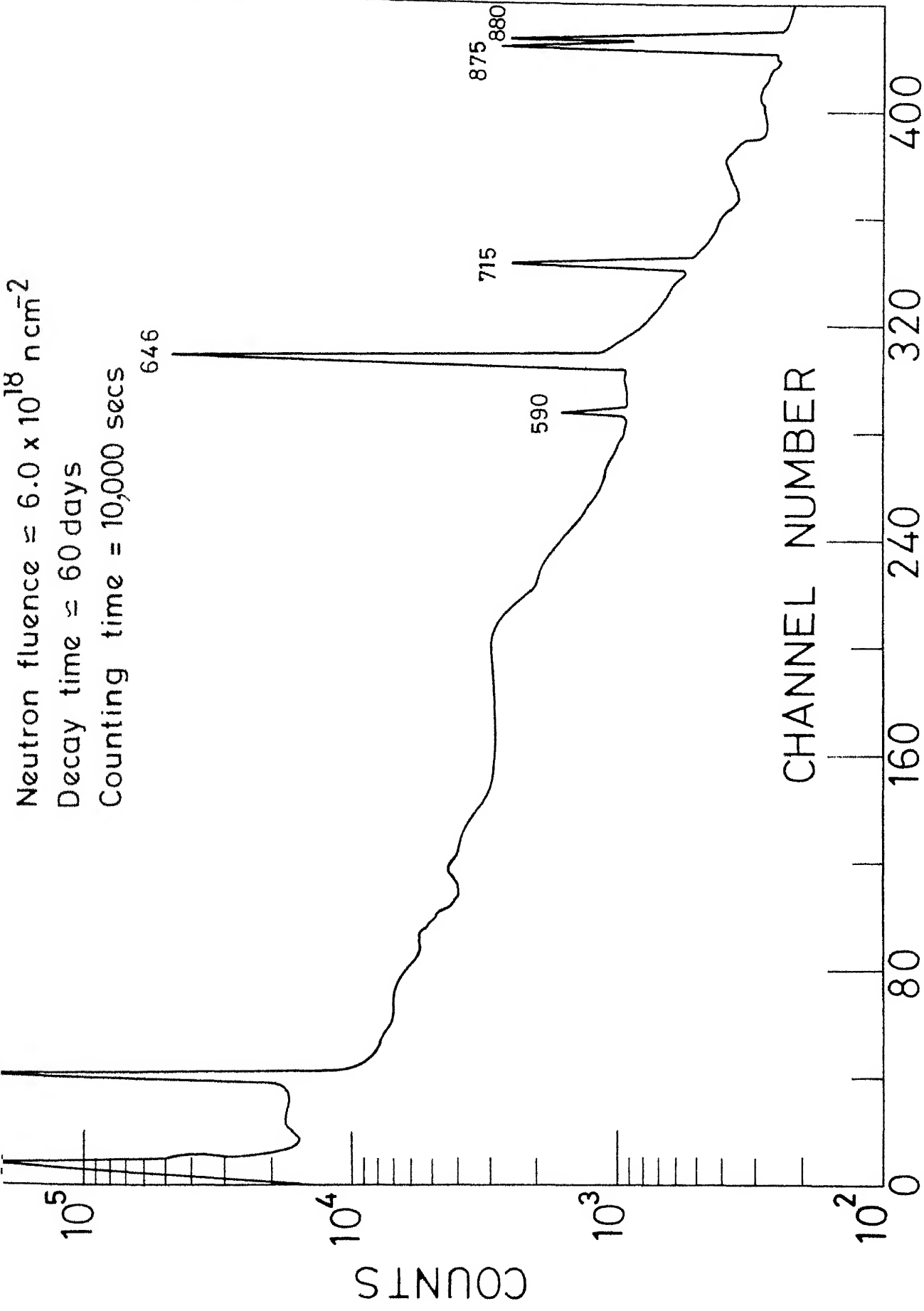
Fig. 2.9   ϒ-spectrum of radiochemically separated Osmium.

pure Ge detector, coupled to 1024 channel analyzer. A typical spectrum is shown in Fig. 2.9. Only ^{185}Os and ^{191}Os energies are observed, which shows the good radio-chemical purity of the separation. Samples were counted for periods of 3-12 hrs. Reproducibility has been checked by repeated counting.

2.9.6 <u>Calculations</u> : The peaks 129.0 Kev (^{191}Os) and 646.0 Kev (^{185}Os) have been used for computing the relative activities. Decay corrections have been applied for the ^{191}Os peak, during the counting period. The activity ratios of all the samples are intrapolated to the same time base by multiplying with proper decay factors, for both the nuclides.

2.9.7 <u>Errors</u> : Only statistical errors due to counting are considered and are computed by simple statistical laws. Identical geometry and counting conditions have been employed in all cases which eliminate relative errors. Errors ranged (at 1σ level) from <1 percent for the most active sample to 6 percent in the case of the weakest sample [Refer Chapter 5 for results].

CHAPTER 3

STUDIES ON TEKTITES AND NATURAL
GLASSES

3.1 Introduction

Tektites are pieces of natural glass ranging in size from microscopic grains to masses weighing tens of kilograms. Most tektites are dark brown in transmitted light, but some are olive brown and others are various shades of green. Tektites are found scattered on the surface of the ground or mixed with geologically young sediments in four major geographic areas. Each geographic area, called a strewn field, is populated by tektites of the same age. Description and details of the known strewn fields and their ages are given in Table 3.1. Microtektites ($<$ 1 mm diameter tektites) belonging to the Australasian, Ivory coast and North American strewn fields have been recovered from deep sea sediments (Glass, 1969, 1972a; Glass et al., 1973). Together with microtektites, the tektite strewn fields cover about 10 percent of the Earth's surface (Glass et al., 1979).

3.1.1 Physical and chemical characteristics of tektites

Tektites occur in four general classes of form as described below.

1) Microtektites : These are usually less than 1 mm in

Table 3.1   Ages of tektites and associated
            craters

Tektite group	Age (M.yr)
Australasian tektites	0.70 ± 0.06
Ivory coast tektites	1.08 ± 0.10
Moldavites	14.7 ± 0.4
North-American tektites	34.6 ± 0.7
Irghizites	1.07 ± 0.06
Associated craters	
Zhamanshin	1.07 ± 0.05
Popigai	30.5 ± 1.2
Elgygytgyn	4.52 ± 0.11
Ries	14.7 ± 0.4
Bosumtwi	1.04 ± 0.11

From Storzer and Wagner, 1977.

diameter, and have been found so far only in ocean-bottom cores. They are clearly associated, in composition and geographic location, with other tektites (Glass et al.,1979).

2) <u>Muong Nong type tektites</u> : These are blocky in shape and layered in structure. These type of tektites are common to all the strewn fields (Barnes, 1964).

3) <u>Splash form tektites</u> : These form the great majority of all known tektites. They look like congealed drops of some viscous liquid. They are shaped like spheres, drops, dumbbells, hamburgers, etc.

4) <u>Flanged buttons and related forms</u> : These are found principally in Australia. The central part or core, is typically lens shaped. Around the edge there is, in some well preserved specimens, a flange formed by glass dropped off the anterior surface presumably by the air stream.

Tektites are similar in their major and trace element contents and isotopic ratios to common type of terrestrial sedimentary rock (Barnes, 1940; Urey, 1958; Hawkins, 1960; Schwarcz, 1962; Taylor and Kaye, 1969). Tektite composition has been compared to loess by several investigators (Vogt, 1935; Taylor, 1962; Sun, 1963). However, there are two obvious differences between the terrestrial rocks and tektites; the water content and the oxidation state of iron. Terrestrial rocks have water content of 0.5 - 2.0 wt. percent while tektites have 0.01 wt. percent (Friedman, 1958).Whereas

in terrestrial rocks ferric content is substantial, in tektites it is 0.08 wt. percent or less.

3.1.2 Origin of tektites : In nature there are only two processes which can form glass; a volcanic eruption and a hypervelocity impact. In both cases the magma quenches very fast leading to the glassy state. Tektites must have formed in either of the two processes and there is no dispute about it. The problem is only about the place of origin, terrestrial or extraterrestrial. Absence of detectable amounts of ^{26}Al ($t_{\frac{1}{2}} = 0.7$ my), a cosmic ray produced nuclide, in tektites, (Viste and Anders, 1962) restricts the choice to the earth-moon system for the place of origin of tektites. Both schools of thought, one supporting the lunar origin (Chapman, 1971; Cameron and Lowrey, 1975; O'Keef, 1976, 1978, 1980; Futrell, 1980) and the other supporting the terrestrial impact (meteoritic/cometory) origin (Spencer, 1933a,b; Cohen, 1963; Urey, 1963; Faul, 1966; Taylor, 1973, 1975; Lin, 1966; King, 1977; Crawford, 1979), exist.

Proponants of lunar origin mainly base their arguments on the extent of strewn fields and the aerodynamic sculpturing of the tektites. On the other hand, the proponants of terrestrial origin do so on the basis of chemical characteristics. O'Keef, 1976 has reviewed both the viewpoints.

With the advent of Apollo mission and access to lunar samples, the lunar origin is loosing ground (Taylor, 1973,1975).

Lack of volcanic activity on the moon and the absence of a glassy sample of tektite composition on the lunar surface (from the areas surveyed) are strong points against lunar origin. The similarity claimed, between 12013 and Javanites in major element composition (O'Keef, 1970) has been thoroughly refuted by Showalter et al., 1971 from a detailed analysis of minor and trace element contents and they stated that 'the rock is not related to tektite glass'.

All the available experimental data render support to the terrestrial impact origin. Chao et al., 1962, 1964 found nickel-iron spherules containing schreibersite and troilite in South-east Asian tektites. These are common minerals in most meteorites. Coesite, a shock indicating form of SiO_2 has been identified in a Muong Nong (M.N.) type tektite by Walter, 1965. Zircon, chromite, rutile, monazite and corundum, all of which are common for sedimentary rocks have been identified in M.N. type tektites (Glass, 1970a, 1972b, Glass and Barlow, 1979) and most of these minerals have shown shock metamorphism. A meteoritic impact on terrestrial sedimentary rocks can produce tektites with all the above characteristics. The atmospheric composition of the gases from the tektite bubbles (Müller and Gentner, 1968; Jessberger and Gentner, 1972; Hennecke et al., 1975) further strengthens the terrestrial origin of tektites.

Although the terrestrial impact origin of tektites has

been well accepted, the identification of the source craters
for the various strewn fields has not been fruitful as yet.
For the oldest known North-American group of tektites no
obvious connection with an impact crater has been traced,
though Popigai Crater in Siberia has been suggested by
Dietz, 1977a,b. The moldavites are identified as coming
from the Ries impact structure of identical age, but the
precise source rock is yet to be identified. The Ivory
coast tektites and the Bosumtwi Crater in Ghana are the
best known association both chemically and isotopically
(Schnetzler, et al., 1967; Kolbe et al., 1967). The
recently discovered tektites, irghizites, (Florensky,
1975, 1977) with their associated impactites (zhamanshinites)
having a close resemblence with them, have an age of 1.07 my.
(corrected fission track age) (Storzer and Wagner, 1977,1979)
which is the generally accepted age of the Australasian
strewn field (0.7 my.). The above evidence led Glass,1979
to suggest that the zhamanshin Crater was the source for the
Australasian tektites, though however, the Zhamanshin stru-
cture may be too small to be a viable source for the Australa-
sian tektites. Other probable sources suggested for the
Australasian strewn field include Elgygytgyn Crater in
Siberia (Dietz, 1977a)and a crater from Cambodia (Hartung and
Rivolo, 1978, 1979). The determination of fission track age
of the craters, Elgygytgyn, Popigai and zhamanshin

(Storzer and Wagner, 1979) (See Table 3.1 for ages) refutes the claim, that these craters are the sources for Australasian/or North American tektites.

Another serious problem that remains to be solved, in the terrestrial origin, is how in such very short time (few seconds) available during impact, the bed rock is molten, homogenized and solidified into bubble free glass, and hurled thousands of kilometers away. The answers to these questions should await our proper understanding of the cratering dynamics (O'Keef, 1980; Taylor and McLennan, 1980).

3.1.3 <u>More about Muong Nong type tektites</u> : The Muong Nong (M.N.) type of tektite glass was first described by Lacroix, 1935 from a locality a few kilometers South of Muong Nong, Loas, where the tektites occurred at a depth of about one metre. The blocky chunks at this locality are unlike the splash forms common in other tektite groups. A study of the internal features of the M.N. type indochinites and of their chemical composition, as compared with the lateritic materials with which they are associated furnishes strong evidence that they are the result of fusion of the ground before laterization (Barnes and Pitakpaivan, 1962). Abundant detrital crystalline mineral grains have been found in layered M.N. type indochinites from Nong Sapong, Northern Thailand. These grains are an integral part of some tektite layers, and their presence furnishes strong evidence that indochinites as

well as other tektite groups in which layered specimens
occur, formed from surficial earth materials (Barnes, 1963).
Also mineral inclusions occur preferentially in M.N. type
tektites with high silica content (low refractive index)
and all of the minerals recovered show evidence of shock
metamorphism (Glass and Barlow, 1979). This supports the
hypothesis that tektites were formed by impact melting.
Variability in the relative abundance of mineral grains
from specimen to specimen indicates some degree of heteroge-
neity in the parent material (Glass and Barlow, 1979).
Walter (unpublished results quoted in O'Keef, 1976)
analysed the polished sections of all types of tektites
by electron microprobe and finds inhomogeneity only in
the case of M.N. type of tektites, where the metal oxide
contents (FeO, Al_2O_3, MgO, CaO and K_2O) inversely correla-
ted with SiO_2 content. Futrell, 1977 finds a remarkable
similarity between the exposed internal structure of M.N.
type tektites and the typical flow structure formed in
extruded terrestrial volcanic glass fragments and believes
in a volcanic origin for these tektites and necessarily a
non-terrestrial one (Futrell, 1980) to account for the very
low water content of these tektites.

3.1.4 <u>Irghizites</u> : Florensky, 1975 has recently identified
new type of tektite and possibly a new occurrence in the
Zhamanshin structure located near the Irghiz river in
Kazakhstan. He gave them the name 'Irghizites'. These

tektites are found associated with impact melts (zhaman-
shinites) which range from nearly 100 percent glass to
greater than 50 percent crystalline material (Florensky
et al., 1977). Two types of Irghizites (acidic and basic)
and two types of zhamanshinites, Dense glass (acidic) and
Vescicular glass (basic) have been identified in the
zhamanshine structure. The acidic irghizites are dense
black glass objects of high silica content $74 \pm 1\%$,
and occur in the greatest numbers (Florensky et al., 1977).
These exhibit flow structure (Ehmann et al., 1977) and often
tektite like primary flight forms. The basic irghizites
are black and vesicular and have a more basaltic composition
with silica content of $54 \pm 1\%$. These are similar in
texture to the M.N. type tektites. In thin section the
basic irghizites are often banded with altering glassy and
partial crystalline 'layers' and xenocrysts of quartz and
feldspar are occassionally found (Florensky et al., 1977).
Texturally and in major and trace element chemistry
(Philpotts et al., 1977; Taylor and McLennan, 1979;
Fredriksson et al., 1977) the basic irghizites are similar
to the Vesicular glass (the basic impact melt from zhamanshin
crater). No satisfactory parent has yet been found for the
siliceous irghizites (Fredriksson et al., 1977).

Irghizites have mostly bulk composition similar to that
of average tektite, but also show some significant differences

from previously analysed land tektites (Ehmann et al., 1977; Fredriksson et al., 1977; Philpotts et al., 1977; Taylor and McLennan, 1979). Also the water content and the Fe^{3+}/Fe^{2+} ratio is higher in the irghizites than in normal tektites (King and Arndt, 1977).

3.1.5 Obsidians : An obsidian is a volcanic glass. Glass is a very common constituent of acid lavas. Silicate melts (magmas) of high SiO_2 content are much more Viscous than their more basic counterparts (basalts) and consequently, cooling of the liquid often restricts the migration of ions, that crystallization virtually ceases, yielding the glassy rock known as obsidian. Flow banding in obsidian is often accentuated by trains of minute crystals (crystallites) of feldspar, amphibole, pyroxene and other minerals or by alternating layers of glass and finely crystalline rock, all of which may enclose larger crystals (phenocrysts) of feldspar, quartz and ferromagnisian minerals (Jack, 1976). It has been shown that obsidian from the same flow or series in the same. volcanic centre are essentially identical in composition and obsidian from various centres may be distinguished by their minor and trace element composition (Jack and Carnichael, 1969). Obsidian is almost completely limited to younger volcanic rocks of late tertiary (Pliocene) to recent age due to the physical instability of the glass (Jack, 1976).

The chemical composition of most obsidians lies in
the range of about 68-77% SiO_2 and 12-15% Al_2O_3 with upto
about 5% Na_2O and 5% K_2O and usually less than 2% Fe_2O_3,
FeO and CaO. Other elements are almost invariably present
in concentrations of less than one percent (Ericson et al.,
1975; Jack, 1976). Partial chemical analysis of obsidian
from many of the occurrences have been reported by several
workers (Parks and Tieh, 1966; Gordus et al., 1968; Jack
and Carmichael, 1969 and Stevenson et al., 1971).

3.2 <u>Objectives of the Present Work</u>

Study of the chemical composition of tektites can
provide evidence about their parent material provided that
the composition of the parent material has not been seriously
modified by the melting process. The close similarity bet-
ween Henbury impact glass and the underlying subgreywake
(Taylor and Kolbe, 1965) Aouelloul glass and zli sandstone
(Cressy et al., 1972) Lonar crater glass and the underlying
core basalt (Stroube Jr. et al., 1978) in chemical compo-
sition clearly demonstrates that the process of melting
does not modify the composition of the parent material. The
occurrence of tektites and impactites in association at
zhamanshin (Florensky, 1975, 1977) is unique and suggests
a genetic relation between them. We have analysed irghizites
and zhamanshinites for N,Li and other trace elements to
understand their relation.

With the discovery of the microtektites the strewn field of the Southeast-Asian tektites extends and covers about 10% of the earth's surface (Glass et al., 1979). Tektites from different localities within the Australasian strewn field show variations in both physical and chemical characteristics (Chapman et al., 1964; Chapman, 1971; Chalmers et al., 1976; Mason, 1979). In a flanged australite, Glass, 1970 observed variations in the major elements with SiO_2 ranging from 60-85% and Al, Fe, Mg, Ca, Na, Ti, Mn and Ba contents varying inversely with SiO_2 whereas K and P varying directly with SiO_2. Such wide variations in chemical composition in an individual tektite specimen are only known in M.N. type tektites (Glass, 1970b and Walter, 1967). Walter has analysed a polished surface of the M.N. type tektite using electron microprobe, for major elements. He attributed the inhomogeneities found, to different compositions of the glass in different layers. In the present work we have studied N, Li, Fe, Cr, Co, Sc, Hf, Ta, Ce, Eu, Tb and Cs in a layered M.N. type tektite, in a systematic way, to understand the cause of the inhomogeneities and possible implications.

Obsidian glasses from Lipari, Italy and Glass Mountains, California, have also been studied to understand the composition of the volcanic glasses and compare it with tektites and impactites. The possible implications towards the volcanic origin of tektites can be traced from this comparison.

The description and sources of the samples studied are given in Table 3.2.

3.3   Results and Discussions

3.3.1   Muong Nong tektites : The purpose of the investigation was to find the trace element distribution in various layers of a M.N. type tektite. As shown in Fig. 3.1a, 3 slices were cut from a layered M.N. type tektite, in a direction perpendicular to the layering. The slice 1 (Fig. 3.1b) was cut into 9 pieces of approximately equal width along the layering direction. These pieces are numbered 1,2, ... 9 from the base. Each of these pieces represent a group of layers of the tektite and numbered TL-1, TL-2, ... etc. (Thin layer-1, etc.). Slice 2 was similarly sliced into 9 pieces along the layering direction so that each piece represents again a bunch of layers. From these, alternate pieces 2,4 and 6 were selected for analysis. Each of these pieces L2,L4 and L6 were further cut into pieces(shown in Fig. 3.1c)and numbered as L2a,L2b etc. meaning layer 2 piece a etc. The nine pieces from slice 1 will facilitate the investigation of trace elements in various layers, whereas the pieces L2a, L2b etc. facilitate the investigation within a layer. Another slice 3 was cut at a distance apart (one end of the specimen). This was cut into 4 layers, each layer being further cut into 4 pieces a,b,c,d as shown in Fig. 3.1d. The investigation of these samples from slice 3 will give an indication of how heterogeneous is the tektite within a few centimeters apart.

Table 3.2   Sources of the various samples

Sample No.	Description	Source
USNM 5938 3-10	Irghizite group III (Acidic)	Smithsonian Institution
USNM 5939 10	Irghizite group IV (Basic)	-do-
-	Zhamanshinite (Acidic) Dense glass	-do-
-	Zhamanshinite (Basic) Vesicular glass	-do-
-	Australite	Dr. Kohman
T-5-6	Moldavite	-do-
-	Muong Nong type tektite	Dr. Futrell
-	G-2 obsidian,Stakkahbidraur Lodumundrafford,Ostisland	Dr. Kohman
	G-4 obsidian, Irridescent Lipari, Italy	-do-
	G-5 obsidian, with Segregation zones Anuacalde,Lipari,Italy	-do-
	G-10 obsidian,Lipari,Italy	-do-
	G-11 obsidian,Glass Mountains Inyocounty, California.	-do-
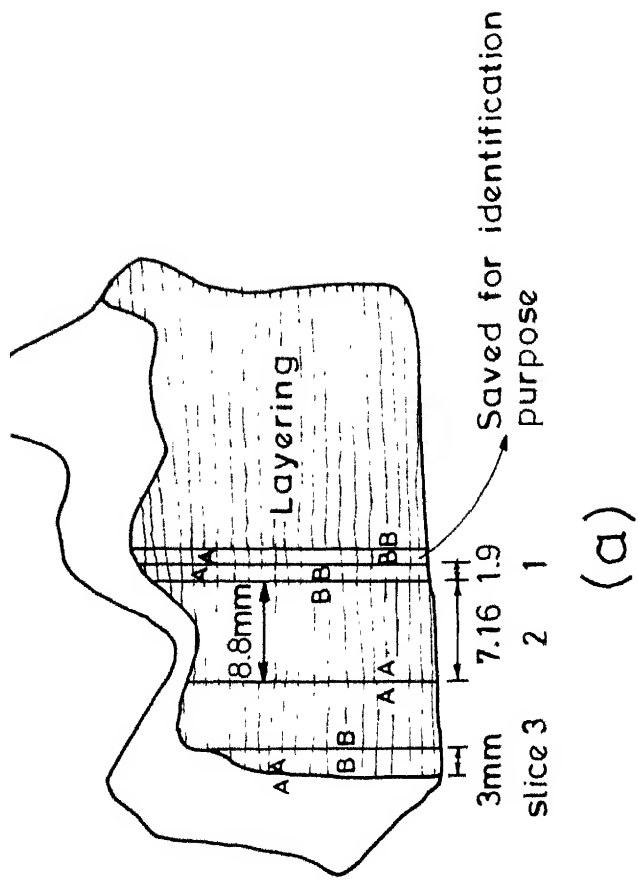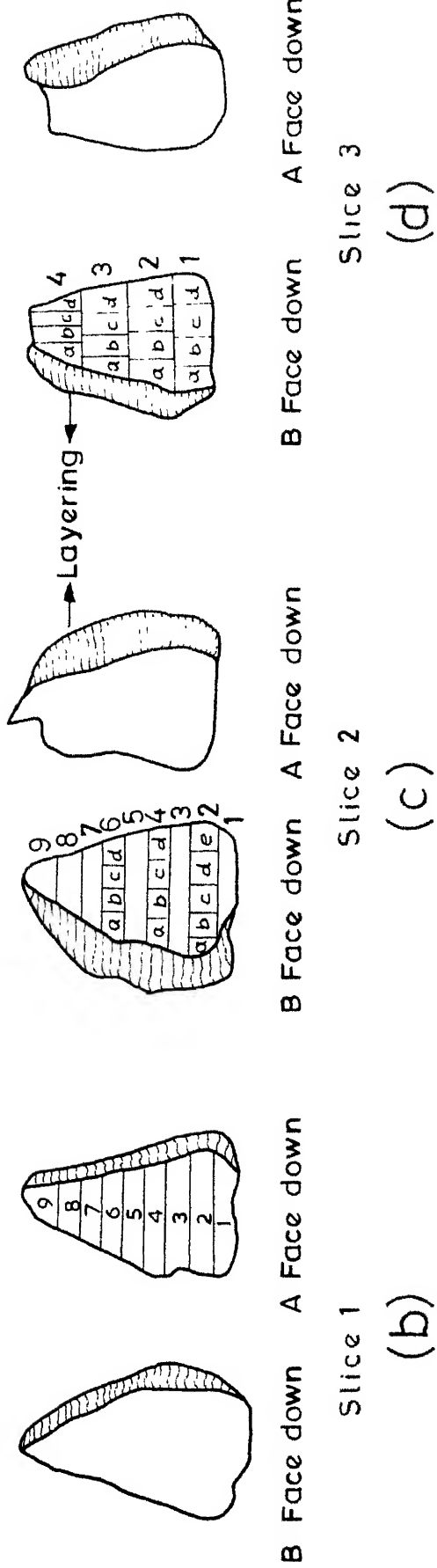
Fig. 3.1 Layered Muong Nong type tektite and the position of the slices.

(a)

Layering

Saved for identification
purpose

3mm

8.8mm

7.16 1.9

slice 3   2   1

(b)

B Face down   A Face down

Slice 1

(c)

B Face down   A Face down

Slice 2

Layering

(d)

B Face down   A Face down

Slice 3

The results for the slices 1,2 and 3 are respectively shown in Table 3.3, Table 3.4 and Table 3.5. In case of slices 1 and 2 we could get 12 elements (FeO,Cr,Co,Sc,Ta,Hf, U,Eu,Th,Cs,N,Li) whereas for slice 3 we could get only 8 elements (FeO,Cr,Sc,Co,Eu,Cs,N,Li) because of the larger cooling time for slice 3 samples. Trace element data for A.N. type tektites are not available for a comparison. As can be seen there are variations for all the elements analysed here, in various layers and also within a layer. These variations are much more pronounced in slice 3 samples than the rest, which shows the variation in the degree of heterogeneity in the sample.

For a better appreciation of the variations the data for each layer of slices 1 and 3 are normalized to the grand mean of that slice for each element and the normalized values are plotted in Fig. 3.2 and Fig. 3.3. It can be seen that the deviations with respect to the mean value are quite irregular for all the layers and there is no pattern. But the deviations are much more pronounced for slice 3 compared to slice 1. Most of these deviations are beyond the errors in measurements (See relative errors in Table 3.4 and Table 3.5). This shows complete heterogeneity in the tektite sample with respect to all the elements studied here.

From the data of slices 2 and 3 (Table 3.4 and Table 3.5) similar plots like Fig. 3.2 and Fig. 3.3 can be drawn to show

Table:3-3 Data for slice 1 of the M.N. type tektite
(Tl: Thin Layer)

| Element | Sample | | | | | | | | | Mean | Abs. Err.(%) | Rel. Err.(%) |
	Tl-1	Tl-2	Tl-3	Tl-4	Tl-5	Tl-6	Tl-7	Tl-8	Tl-9			
Feo(%)	3.2	3.5	3.4	3.3	3.4	3.1	3.5	3.5	3.6	3.4	0.7	0.8
Cr	124.9	134.5	130.3	125.4	126.4	119.3	139.1	136.2	134.5	130.7	23.6	2.8
Co	13.3	14.3	13.9	13.6	14.3	13.3	15.0	14.5	15.0	14.2	1.3	1.4
Sc	12.1	13.3	13.1	12.6	12.8	11.9	13.4	13.3	13.7	12.9	0.3	0.3
Ta	1.4	1.5	1.7	1.8	1.2	1.3	1.6	1.5	1.7	1.5	19.5	10.9
Hf	7.0	7.8	7.6	7.9	7.4	7.3	7.9	7.8	8.1	7.7	2.9	1.5
Ce	55.8	58.9	58.5	58.4	59.3	54.1	60.4	60.1	60.0	58.7	1.7	1.0
Eu	1.4	1.5	1.5	1.5	1.5	1.4	1.6	1.6	1.6	1.5	2.1	1.6
Tb	1.3	1.3	1.3	1.4	1.3	1.3	1.4	1.3	1.4	1.3	6.7	4.1
Cs	4.9	5.3	5.3	5.1	5.2	4.8	5.4	5.4	5.3	5.2	15.9	2.1
N	43.0	43.4	52.5	47.8	47.2	47.7	42.6	47.2	48.9	47.1	10.0	5.0
Li	53.8	49.2	51.3	53.0	54.6	53.8	56.0	53.7	53.1	53.5	10.0	0.5

Table:3-4 Data for slice 2 of the M.N. type tektite

Element	Sample													Err.(%)
	2La	2Lb	2Lc	2Ld	2Le	4La	4Lb	4Lc	4Ld	6La	6Lb	6Lc	6Ld	
Feo(%)	3.1	3.2	3.4	3.3	3.2	3.2	3.2	3.0	2.9	3.1	3.1	3.1	3.0	0.7
Cr	111.1	114.1	126.3	114.2	110.9	118.3	120.9	106.8	99.6	106.1	108.2	109.8	106.0	23.6
Co	13.7	13.5	14.7	13.8	13.6	13.2	13.7	12.7	12.2	13.0	13.2	13.2	12.9	1.3
Sc	11.9	12.0	13.0	12.5	12.3	12.2	12.4	11.7	11.1	11.8	11.7	11.7	11.3	0.3
Ta	1.1	1.2	1.1	1.2	1.1	1.1	1.2	1.1	1.1	1.2	1.0	1.2	1.0	19.5
Hf	7.8	7.6	8.2	7.7	7.5	7.7	8.1	7.4	7.2	7.3	6.7	6.9	6.5	2.9
Ce	73.8	70.6	79.4	74.2	72.3	76.0	74.7	70.1	68.5	88.0	70.5	67.7	64.4	1.7
Eu	1.5	1.4	1.6	1.5	1.4	1.4	1.5	1.4	1.4	1.4	1.3	1.4	1.3	2.1
Tb	1.3	1.3	1.4	1.4	1.4	1.5	1.4	1.3	1.3	1.3	1.3	1.3	1.2	6.7
Cs	5.6	5.5	6.1	5.7	5.7	5.6	5.5	5.3	5.1	5.4	5.7	5.4	5.3	15.9
N	19.6	20.9	18.9	18.4	18.8	19.4	21.2	19.6	19.3	19.2	19.9	7.5	17.4	10.0
Li	56.2	52.2	59.3	58.3	58.3	53.2	56.9	55.1	55.7	56.3	56.5	60.2	60.1	10.0

Table:3-5 Data for slice 3 of the M.N. type tektite

Element	Sample																Abs. Err. (%)	Rel. Err. (%)
	1a	1b	1c	1d	2a	2b	2c	2d	3a	3b	3c	3d	4a	4b	4c	4d		
FeO (%)	4.5	3.5	5.2	4.8	11.5	4.6	4.7	5.1	9.1	7.5	10.1	7.3	9.5	8.4	3.9	8.6	30	10
Co	15.0	15.5	14.8	15.0	15.0	14.8	15.5	15.5	17.7	12.4	21.6	20.2	12.6	12.5	15.2	13.7	2	1
Sc	18.8	18.7	18.1	18.2	16.6	18.7	19.1	17.7	21.7	13.2	26.9	25.3	14.5	14.8	19.3	15.1	7	3
Ce	19.0	22.1	18.4	19.6	32.2	19.1	19.1	21.4	43.4	22.0	52.4	52.1	20.6	23.6	20.3	29.1	15	8
Eu	1.4	1.4	1.4	1.4	1.4	1.5	1.5	1.5	1.7	1.2	2.1	2.0	1.2	1.2	1.5	1.4	2	1
Cs	5.0	4.8	4.6	4.8	6.8	4.6	4.8	4.8	7.1	5.5	8.9	8.3	5.8	5.6	4.7	6.20	20	1.5
N	23.3	24.2	24.3	26.3	26.3	20.4	19.8	18.2	19.7	32.0	18.3	18.5	28.8	29.6	18.5	29.0	10	5
Li	58.8	55.2	55.8	58.6	54.2	54.7	56.7	54.3	44.3	56.4	42.5	42.10	54.4	58.3	56.5	54.6	10	0.5
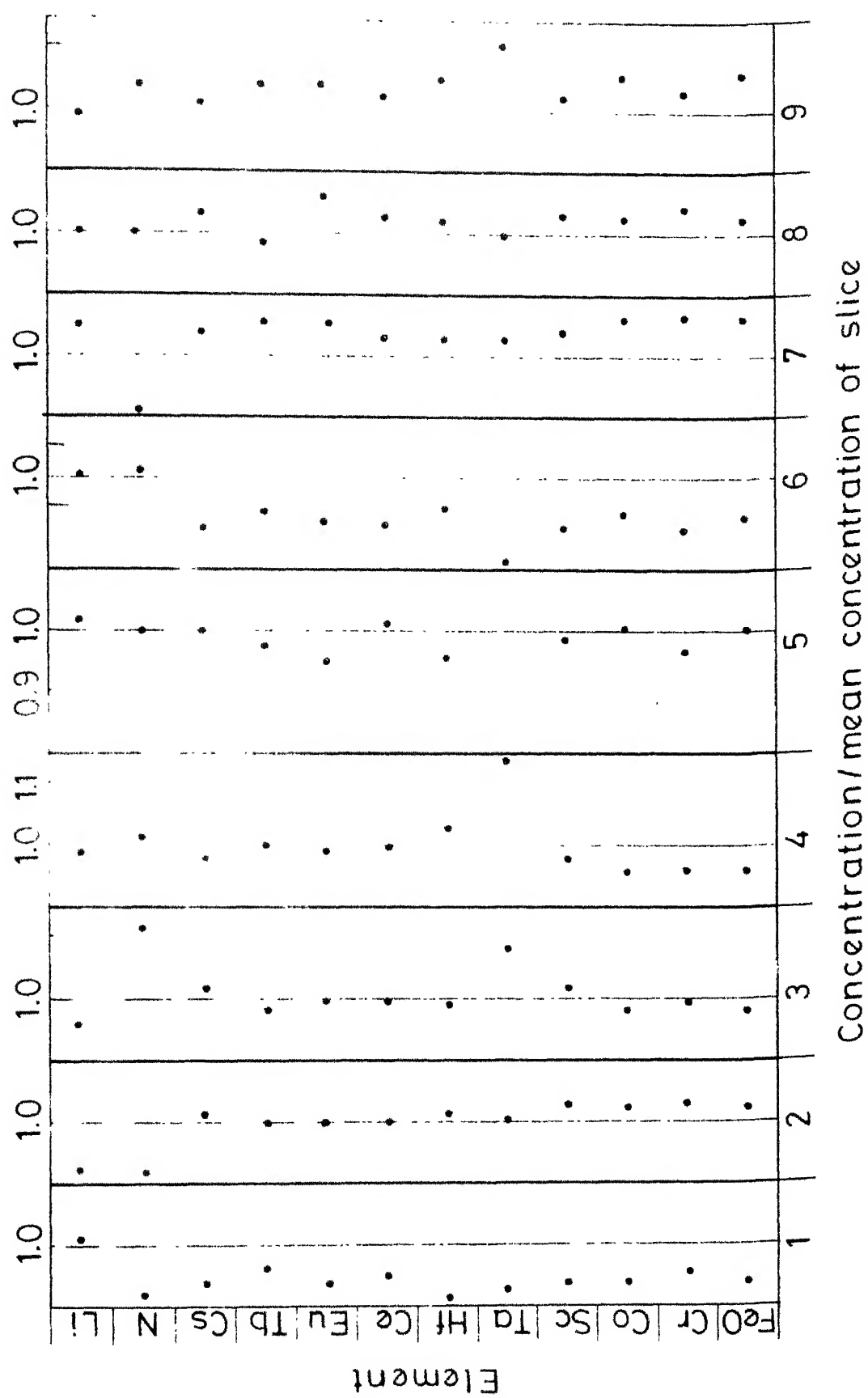
Fig. 3.2   Chemical variations in slice 1 layers.
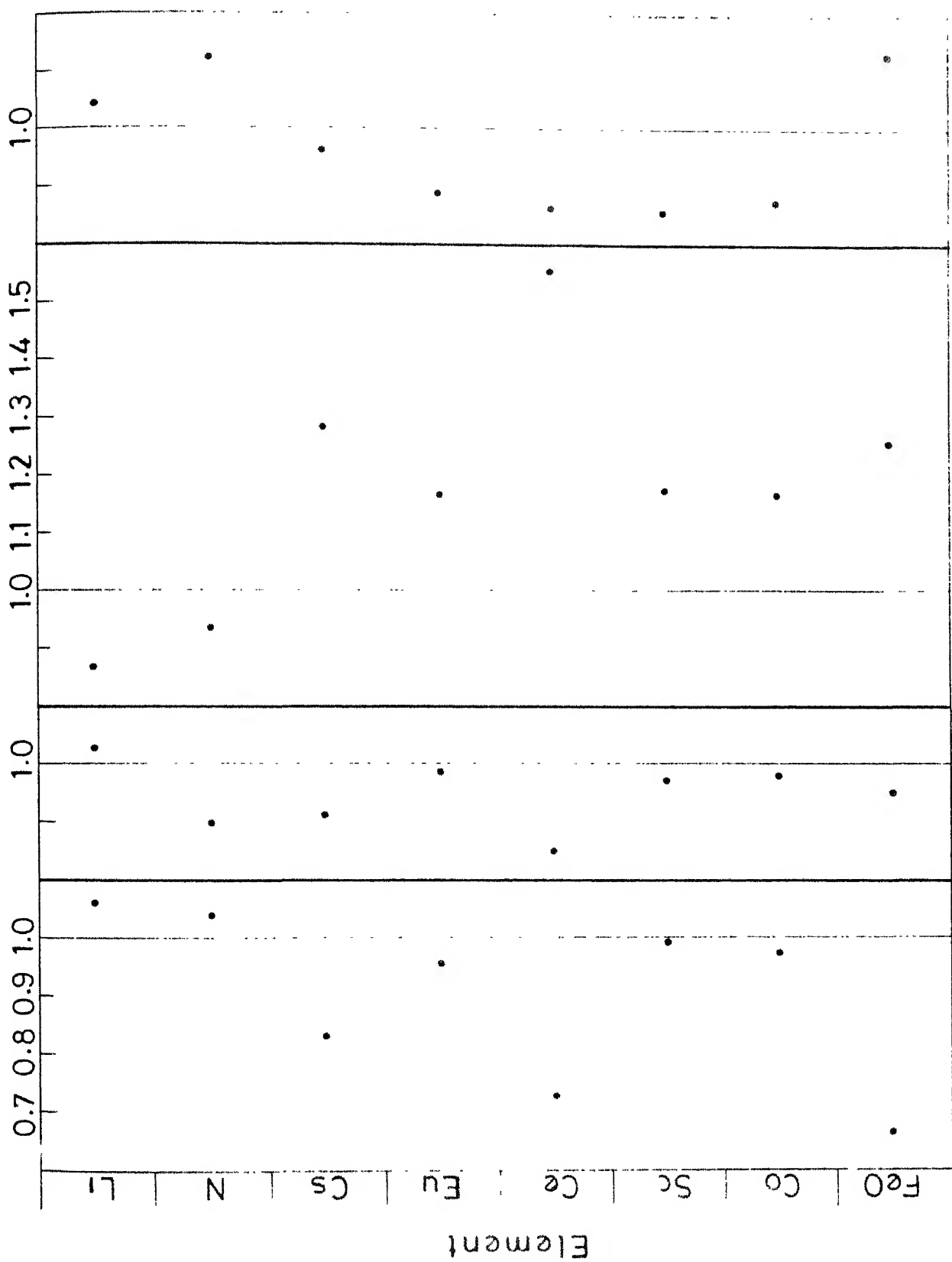
Concentration / mean concentration of slice

Fig. 3.3   Chemical variations in slice 3 layers.

the variation within a layer. In Fig. 3.4 and Fig. 3.5
the variations for layer 2 of slice 2 and layer 1 of slice 3
with respect to their respective mean concentrations are
shown. The plots for other layers look alike. As is
evident from these plots the variations within a layer are
much less compared to the variations between layers. This
emphasizes the fact that the hetrogeneity in the M.N. type
tektites is due to different layers having different
chemical composition.

3.3.2 **Implications** : In relatively thick sections (500 μm)
of M.N. type tektites, Barnes, 1964 identified regions of lens
like shapes, as seen under a microscope, which are a few
tens of micrometers in width and hundreds of micrometers
in length. These are named lenticules and are due to glass
of different refractive index (R.I) than the matrix. Walter,
1976 has shown that the boundaries of the lenticules can be
traced by variations in chemical composition. Glass, 1970a; 1972
has found mineral inclusions in M.N. type tektites and
Glass and Barlow, 1979 have found that only those M.N. type
tektites which have lower R.I. contained the mineral grains.
As refractive index is inversely related to SiO_2 content
(Fig. 2.1 of O'Keef, 1976) and also viscosity is directly
proportional to SiO_2 (at a given temperature) it means that
the mineral grains are present in more viscous layers. Also
Walter, 1967 finds an inverse variation of FeO vs SiO_2 for
M.N. type tektites. Hence, variation in FeO is inversely
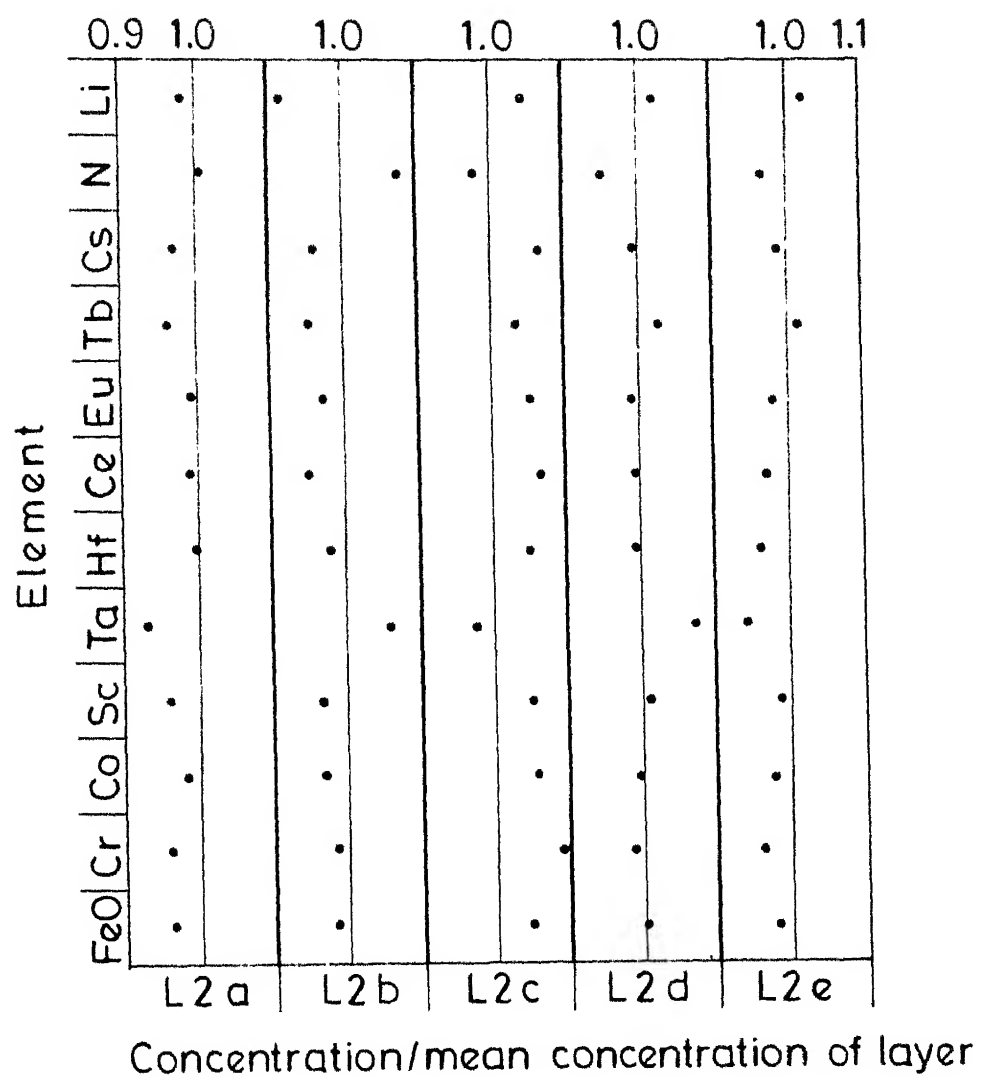
Fig. 3.4   Chemical variations in
layer 2 of slice 2 .
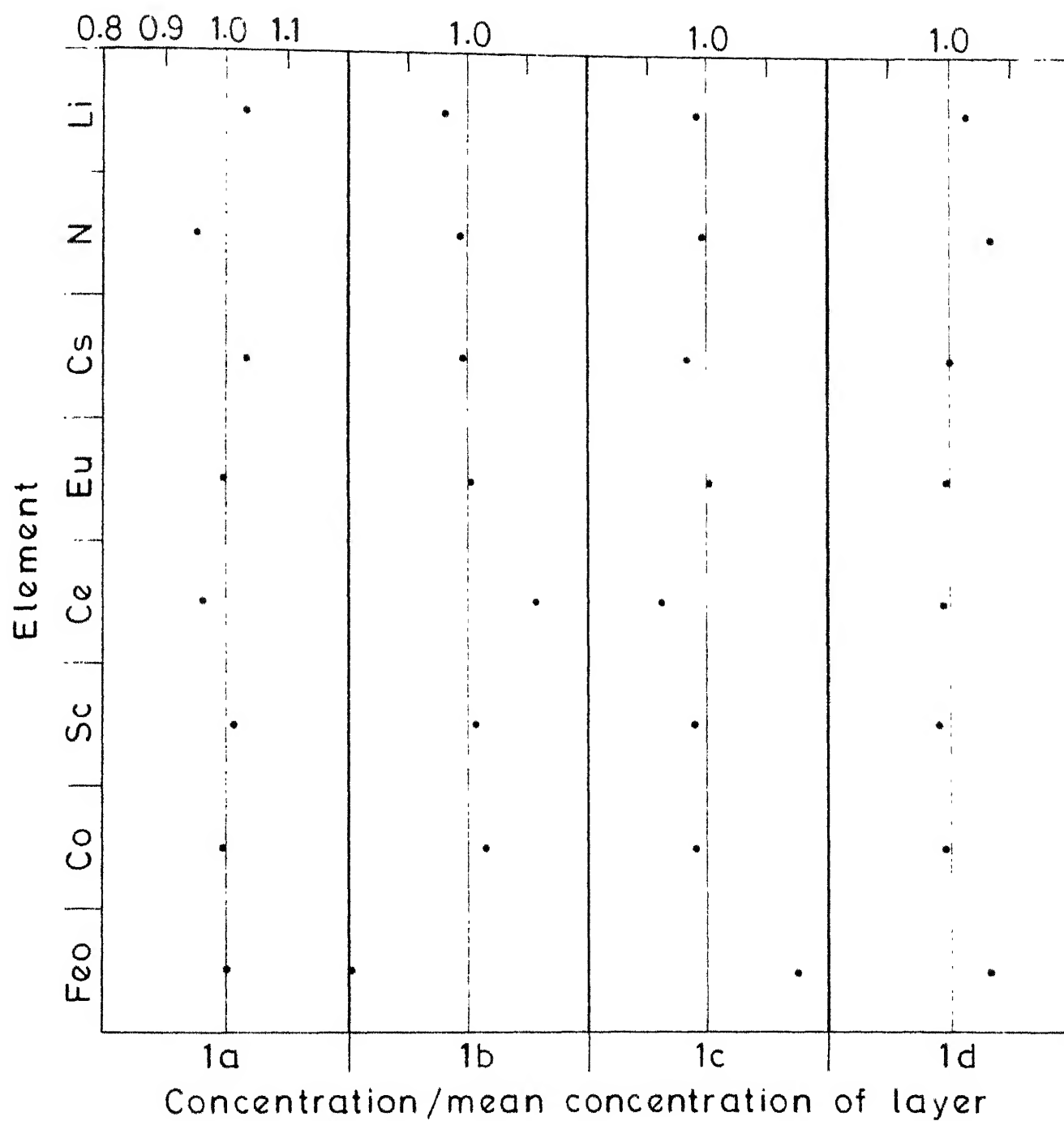
Fig.3.5 Chemical variations in layer 1 of slice 3 .

related to the viscosity of the layer and hence to the
presence of mineral grains. From Fig. 3.2, it can be seen
that for layers 1,6,7 and 9,where the variation of FeO is
more, the variations for all other elements are also more;
whereas for layers 2,3,4,5 and 8,the FeO variation is not
that much and so are the other variations. Same trend is
clear from Fig. 3.3 also. These arguments clearly show the
relation between variations and viscosity and hence to the
presence of mineral grains. Barnes,(1978, quoted in Glass
and Barlow, 1979) also states that 'solar furnace experiments
suggest viscosity may be the controlling factor in deter-
mining whether or not mineral grains are preserved. The
solution and diffusion of included mineral grains is
inhibited in a highly viscous silicate melt, whereas included
minerals dissolve and disperse rapidly in a highly liquid
melt.'

Another important feature in M.N. type tektites, is the
variability in the N content of various slices. In slice 1
N content of all layers is above 40 ppm, in slice 2 it is
less than 20 ppm whereas in slice 3 it is 20-30 ppm. No
other element out of those analysed in this work shows such
uniformly high variation from slice to slice. Shukla et al.,
1979,have found a remarkably uniform N content,about 20 ppm,
in all other tektites and natural glasses and attributed this
remarkable constancy to a sort of equilibration of nitrogen

during melting, above a particular temperature. May be in
the case of M.N. type tektites temperature inhomogeneities
existed at the time of melting and solidification and those
parts which have not attained the equilibration temperature
for nitrogen have retained more N from the source material.
Such a inhomogeneity in N distribution is found in the
impact glasses from zhamanshin. In these zhamanshinites, the
N content varies from 25-154 ppm, whereas in the associated
irghizites N is again around 20 ppm. These impactites are
also enriched in other volatiles (Cs, Tl, Bi and Pb) compared
to the irghizites, further supporting the view that these
impactites have not attained the temperature high enough
for the nitrogen to equilibrate. Enrichment of volatile
elements (halogens, Zn and Cu) in M.N. type tektites compared
to other tektites (Müller and Gentner, 1973) also points
towards less severe heating for the M.N. type tektites
(Becker and Manuel, 1972).

3.3.3 <u>Irghizites and zhamanshinites</u> : Our results on the
irghizites and zhamanshinites are shown in Table 3.6. A
comparison of our values with those of Ehmann et al., 1977
and Taylor and McLennan, 1979 are shown in Table 3.7. Keeping
in view of the fact that different specimens are analysed,
there is a remarkably good agreement. The only discrepancy
is that our Co values for irghizite III and dense glass are
a factor of 2 low and the Hf value for irghizite IV is a
factor of 4 more compared to the Taylor and McLennan values.

Table:3-6 Data for Irghizites and Zhamanshinites

Ele-ment	Irghizite III				Irghizite IV			Dense Glass		Vesicular Glass			Austra-lite	Moldavite		Err (%)
	1	2	3	4	1	2	3	1	2	1	2	3	1	1	2	
Feo (%)	3.0	3.3	3.2	3.1	3.4	3.3	3.6	3.6	3.4	4.3	4.7	4.4	2.3	1.0	1.0	4.5
Cr	186.3	199.4	218.3	195.9	194.7	221.0	263.4	52.3	91.0	32.4	---	47.0	---	27.2	32.1	20.0
Co	53.1	55.8	55.0	53.0	59.2	58.1	60.0	15.3	13.5	16.3	15.8	17.0	9.8	4.7	4.7	2.0
Sc	8.3	8.7	8.9	8.3	8.5	8.5	8.9	14.4	13.3	13.7	13.6	14.4	8.9	4.2	4.0	1.0
Ta	0.8	0.9	0.9	0.7	0.9	0.8	0.9	1.1	1.1	0.2	0.1	0.2	1.2	0.6	0.6	6.5
Hf	6.5	7.3	7.2	6.3	7.3	7.1	7.5	5.6	5.6	1.5	1.5	1.1	6.7	5.9	5.3	10.0
Ce	30.7	26.8	25.3	25.9	29.6	27.2	29.7	44.3	44.7	26.4	33.5	27.3	43.1	35.2	30.8	10.0
Eu	0.7	0.8	0.8	0.8	0.8	0.7	0.7	1.3	1.3	0.9	0.9	1.0	1.0	0.8	0.8	3.5
Tb	0.4	0.4	0.5	0.4	0.5	0.4	0.5	0.8	0.8	0.5	0.5	0.5	0.6	0.4	0.4	6.0
Cs	2.1	2.1	2.2	2.2	2.1	2.4	2.5	5.6	5.9	2.4	2.2	2.4	4.7	13.4	13.3	5.5
N	20.2	22.1	22.7	22.7	---	23.3	25.0	25.1	85.4	154.0	51.2	98.8	18.9	17.9	17.4	10.0
Li	32.2	30.7	31.6	32.4	---	31.5	31.5	64.3	263.4	13.9	13.3	14.7	42.4	44.2	44.2	10.0

Table:3-7 Comparision of data for Irghizites and Zhamanshinites

Element	Irghizite III			Irghizite IV		Dense glass		Vesicular glass		
	This work	T & M[1]	Ehmann et al.[2]	This work	T & M	This work	T & M	This work	T & M	Enmann et al.
Feo(%)	3.1	6.5	4.4	3.4	7.7	3.5	5.5	4.5	4.7	6.0
Cr	200.0	200.0	241.0	226.4	---	71.6	92.0	39.7	22.0	21.0
Co	54.2	102.0	78.0	59.1	----	14.4	16.0	16.4	19.0	19.4
Sc	8.6	9.4	10.3	8.6	----	13.8	15.0	13.9	17.0	16.3
Ta	0.8	---	0.9	0.9	---	1.1	1.0	0.1	---	n.d
Hf	6.8	8.4	8.9	7.3	1.8	5.6	6.3	1.5	1.8	2.2
Ce	27.2	44.7	55.0	28.8	27.7	44.5	83.6	29.0	28.0	24.0
Eu	0.8	0.7	0.8	0.8	1.0	1.3	1.6	0.9	1.1	1.1
Tb	0.4	0.5	---	0.5	0.5	0.8	---	0.5	0.5	---
Cs	2.1	1.9	2.8	2.3	6.6	5.8	7.8	2.4	3.6	6.5

1. Taylor and McLennan 1979 ; 2. Ehmann et al., 1977 ; n.d.= not detected

These differences may be inherent to the sample, in view
of the agreement with the rest of the elements. The N values
for these samples are being reported for the first time.

An examination of the data from Table 3.6, reveals the
following points : 1) irghizites are remarkably homogeneous
in chemical composition as can be seen from the replicate
analysis, 2) zhamanshinites are not homogeneous with respect
to Cr and N at least, out of the elements studied here, 3) Cr
and Co are enriched in irghizites as compared to zhaman-
shinites, probably due to meteoritic contamination. The
Co content of irghizites is the highest value ever found in
tektites, 4) both the acidic and basic irghizites, though
widely differing in major element composition (Fredriksson,
et al., 1977; Taylor and McLennan, 1979) are very much similar
with respect to the elements analysed in this study, 5) the
same is not true for the two impactites, dense glass (acidic)
and vesicular glass (basic). Almost all the elements studied
here, except Co and Sc, have widely differing concentrations
in both the impactites.

Fredriksson et al., 1977 have noted a similarity between
the basic irghizites and the vesicular glass in major element
composition. Taylor and McLennan, 1979 have similarly found
a matching between acidic irghizites and the Javan group of
tektites from the Australasian strewn field. Florensky et al.,
1977 found a texural similarity between basic irghizites and

M.N. type tektites. Hence, it is highly instructive to
compare the compositions of the following. a) acidic
irghizites and Dense glass (Fig. 3.6), b) acidic irghizite
and australian tektite (Fig. 3.7), c) basic irghizite and
vesicular glass (Fig. 3.8) and d) basic irghizites and M.N.
type tektites; basic irghizites and Australasian micro-
tektites, in view of the similarity between acidic irghizites
and australites and the most basic tektites known in Austra-
lasian strewn field, being the microtektites (Fig. 3.9). In
these figures all the elements except FeO (%) are expressed
in ppm units. Except for the microtektite data which we
have taken from Frey et al., 1970 for other tektites we
have used only our data. In all these plots both Co and Cr
points are very much off from the diagonal line due to the
high content of these two elements in both acidic and basic
irghizites. With respect to the other elements a good com-
parison is evident between acidic irghizites and australite,
and basic irghizites and M.N. type tektites as well as
Australasian microtektites. The comparison between basic
irghizites and vesicular glass, acidic irghizites and dense
glass are not quite good, but on a relative basis the
irghizite (basic) vs. vesicular glass plot, where all the
three REE (Ce, Eu, Tb), Cs, Sc and FeO compared well, is
a better match. May be analysis of a large number of samples
will show a more reliable trend.
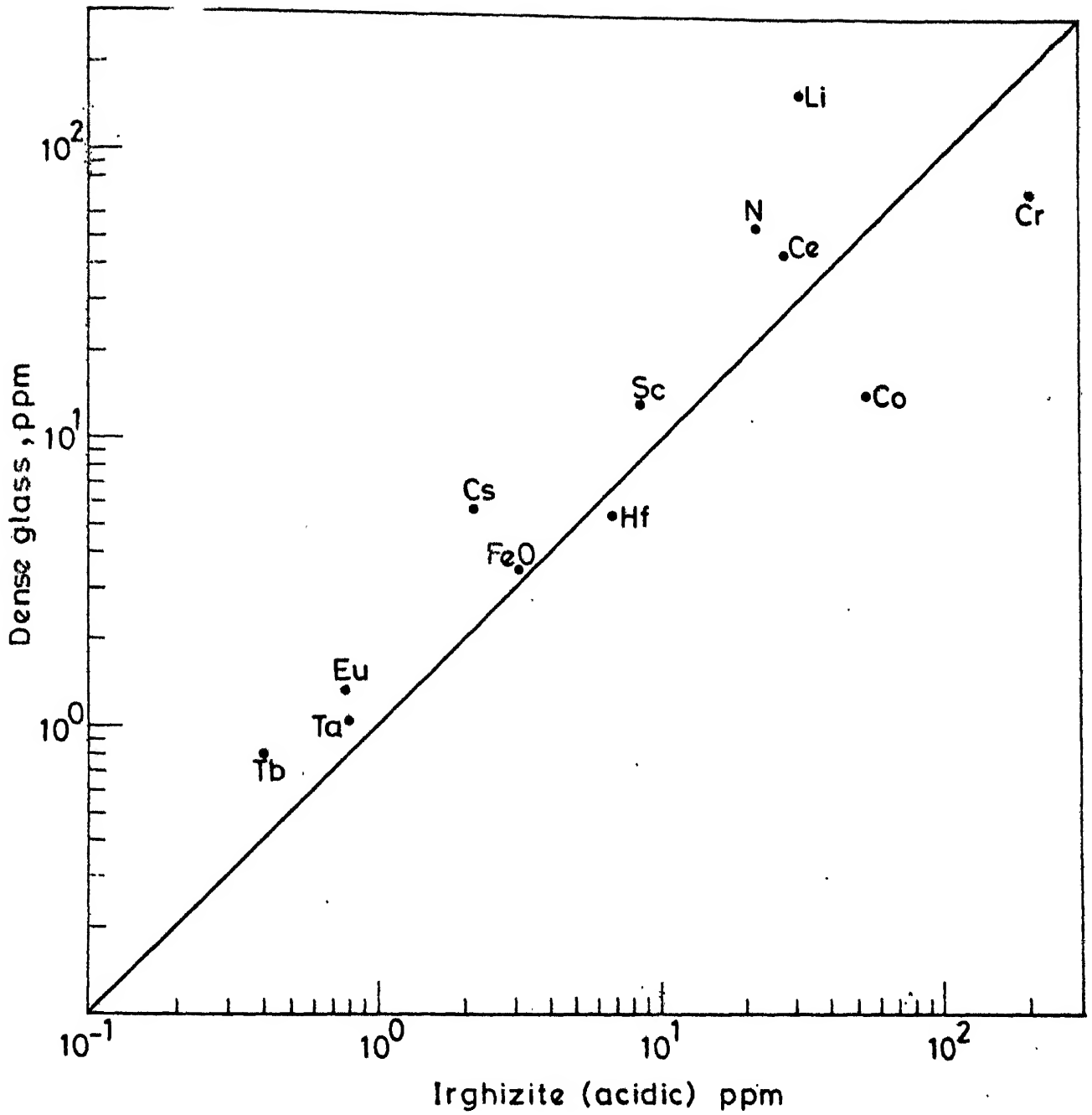
Fig. 3.6   Comparison   of Irghizite(acidic) vs. Dense glass.
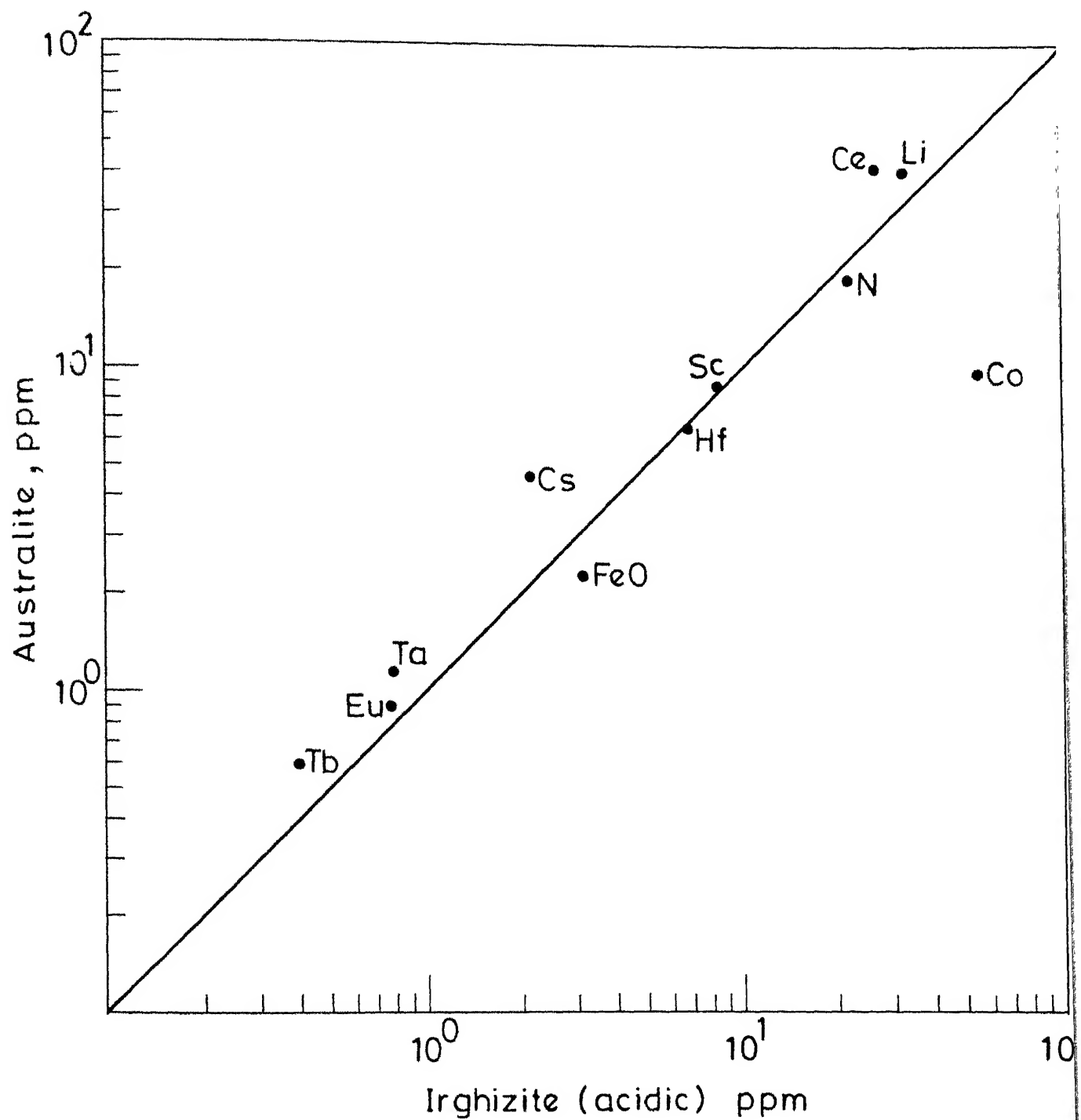
Fig. 3.7   Comparison of Irghizite (acidic) vs. Australite .
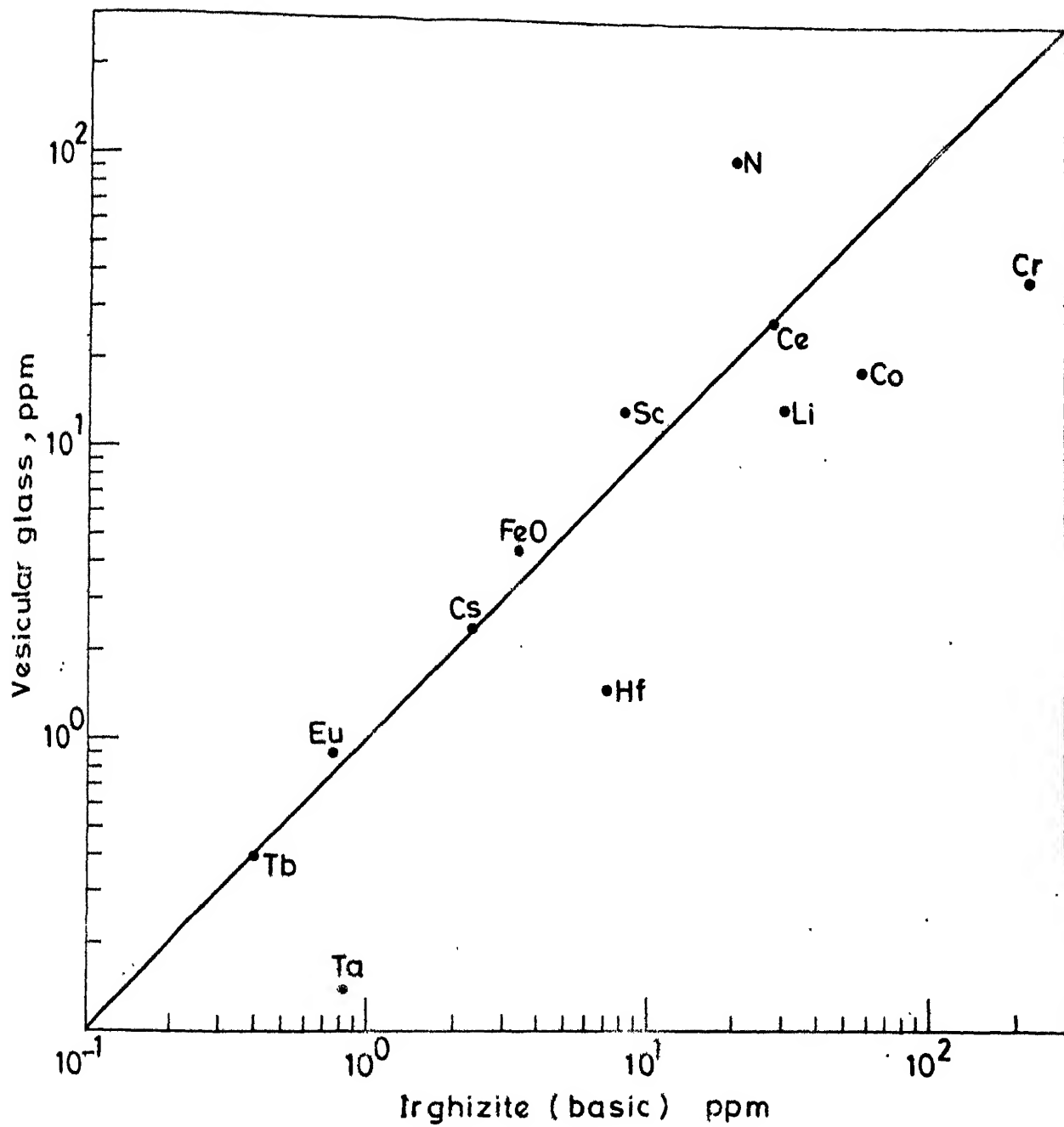
Fig. 3.8   Comparison of Irghizite (basic) vs. Vesicular glass.
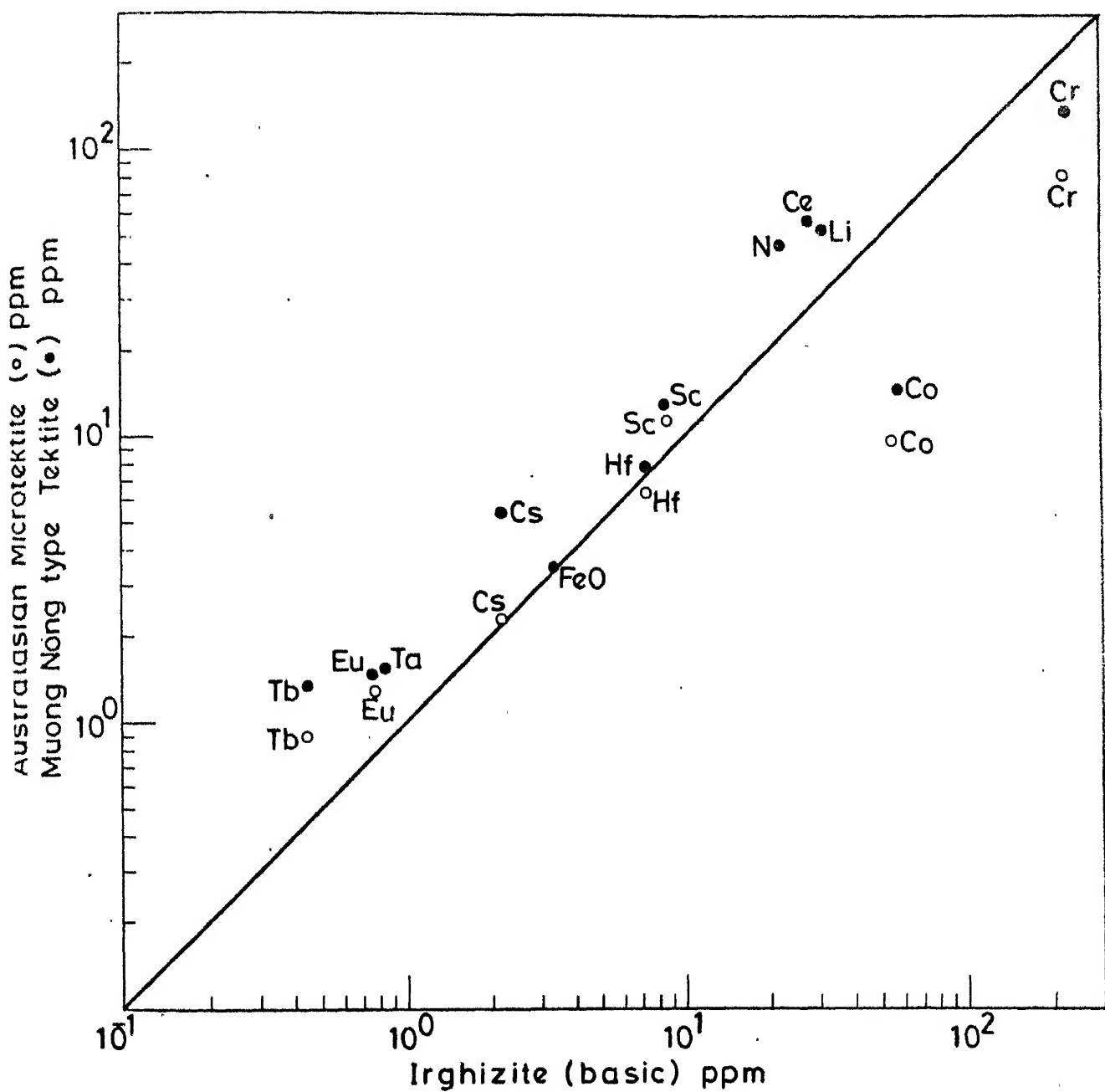
Fig. 3.9   Comparison   of Irghizite (basic) vs. (•) Muong Nong
type Tektite (o) Australasian Microtektite .

3.3.4 <u>Obsidian glasses</u> : In this study we have included the following obsidians G-2, G-4, G-5, G-10 and G-11, the sources for which are described in Table 3.2. Our results are shown in Table 3.8. There is no literature data available for these samples for comparison. However, our values of Ce and Li, for which data are available for some other obsidians, fall in the general range.

The following points can be inferred from the data. . 1) Obsidians from different sources have comparable compositions, 2) in G-5 which is an obsidian with segregated zones, we have analysed the glass portion and the opaque silicate portion separately. As can be seen, both have remarkably same composition. This shows that the process of glass formation from the volcanic lava is only a physical change and does not involve a chemical differentiation. This conclusion is atleast true in the case of G-5. 3) In the process of sealing the samples in vacuum, a part of the piece G-4 got heated by the hand-torch and swollen into a frothy mass. This portion has been separately analysed to understand the chemical differentiation due to heating. Except Co and Cs which are not effected, all the rest of the elements are severely depleted in the G-4 (heated). We cannot conclude much unless a good number of similar experiments are carried on other glass samples.

None of the obsidians analysed here, have an abundance pattern that matches with any of the tektites known. A

Table:3-8 Data for Obsidian glasses

Element	Sample							Error (%)	Literature Dixon(1976)
	G-2	G-4	G-4 (Heated)	G-5	G-5 (Silicate)	G-10	G-11		
Feo(%)	0.9	1.2	0.4	1.1	1.1	1.0	0.6	5.0	
Cr	---	---	---	---	---	---	---	---	
Co	0.1	0.2	0.2	0.4	0.4	0.4	0.1	20.0	
Sc	1.2	3.0	0.4	1.1	1.1	1.1	0.5	3.0	
Ta	5.6	5.1	3.7	2.9	3.1	2.8	5.2	5.0	
Hf	11.7	27.4	3.6	8.0	8.0	8.0	5.3	10.0	
Ce	65.9	58.0	18.9	85.8	91.1	84.6	21.1	10.0	60-75
Eu	2.4	1.7	0.1	0.2	0.2	0.2	0.0	5.0	
Tb	2.6	1.7	0.6	0.9	1.0	0.9	0.8	5.0	
Cs	1.0	3.4	3.9	15.3	15.3	15.2	5.3	5.9	
N	28.0	17.5	---	17.6	16.2	18.0	---	10.0	
Li	3.0	59.0	---	90.0	69.4	77.4	---	10.0	16-180

terrestrial volcanic origin of tektites can very safely be ruled out on the basis of chemistry alone, leaving aside other difficulties. One interesting fact about obsidians also is about the N content, which is again around 20 ppm as in other natural glasses. This shows that in terrestrial environment all the natural glasses (devoid of the process of formation) attain an equilibrium value, above a particular temperature, provided the source rock has enough nitrogen.

3.3.5 <u>Implications regarding parent rock and the origin of</u> <u>tektites</u> : The heterogeneity in the M.N. type tektites points out the hetreogeneity in the source rock. Glass and Barlow, 1979 from the variable abundance of mineral grains in M.N. type tektites also reach the same conclusion. From the similar physical features of M.N. type tektites and obsidian glasses,Futrell, 1977, 1980 suggested lunar volcanic origin for these tektites, which may also account for the dryness of these tektites. From ballistic considerations O'Keef, 1976,1978 and Cameron and Lowrey, 1975 have also suggested a lunar volcanic origin for tektites. Several serious problems, both physical and chemical, including the fact that moon is depleted in hydrogen, the fuel suggested by O'Keef to power the volcano, invalidate the lunar volcanic origin. The obsidians analysed here, exemplify the fact that physical resemblence does not ensure a chemical similarity and pose a serious problem for the volcanic model.

The occurrence of irghizites and zhamanshinites together and the similarity between the basic irghizites and vesicular glass show the genetic relation between the impact glass and tektites. Further the similarity between acidic irghizites and Australasian tektites and basic irghizites and M.N. type tektites both in physical form and chemical composition forge a relation between irghizites and other known tektites. The higher abundance of volatiles in zhamanshinites compared to irghizites shows, the degree of heating to be more for irghizites. A terrestrial impact origin of tektites is in accord with all the above observations. Only problem remains to be solved in the terrestrial impact model is the ballistic one. Fundali and Ford, 1979 have found Darwin glass 20 km. away from the source crater, so that atmosphere has not proved a insuperable barrier for this event. An impact generated atmospheric blast wave has been suggested by these authors for the distribution of Australasian tektites. Remo and Sforza, 1977 have shown that the physical, geochemical and geophysical characteristics of tektites may be explained in terms of the aerodynamics of hypersonic gas flow and the interaction of this flow field with the target material at impact. Further understanding of the cratering dynamics in future may settle the ballistic problem.

CHAPTER 4

STUDIES ON STONE METEORITES

Nitrogen and lithium have been studied in sieve fractions and density fractions of stone meteorites. In some cases Co and Eu have also been analysed on the same sieve fractions, by INAA, before consuming the sample for N,Li determination by RNAA. In Ambapur Nagla and Shalka, hand-picked minerals were studied for N and Li. In Abee, Atlanta, Beardslay, Dhajala, Saratov and Ambapur Nagla, N and Li have been studied in bulk meteorite as well as in chondrules and lithic fragments, wherever possible. In Table 4.1, the classification, and sources, of the meteorites studied have been described. Nitrogen and lithium results are presented separately.

4.1 Nitrogen in Meteorites

4.1.1 Nitrogen in bulk meteorites : Our results on bulk meteorites are given in Table 4.2 and compared with the literature values in Table 4.3. The N data of Moore and co-workers (hereafter referred to as Arizona group) are systematically higher and Müller's numbers are systematically lower than ours. This is expected due to the contamination problems in inert-gas fusion technique of the Arizona group and the incomplete distillation of N in Müller's Kjeldahl method, as discussed in detail in the experimental chapter.

Table 4.1 Sources and other details of the Stone
meteorites included in this study

Meteorite	Abbreviation used in Fig.	Class	Fall or find	Source and Cat.No.
Orgueil	Org	CI1	Fl	Dr.Pellas, # 237
Cold Bokkeveld	Cbw	CM2	Fl	Dr. Lal, TIFR
Murray	Murr	CM2	Fl	Dr.Moore, # 635.2
Murchison	Murc	CM2	Fl	Dr. Kohman
Allende	All	CV3	Fl	USNM 3496
Fayetteville	Fay	H	Fl	Dr.Mason, NMNH,1731
Dhajala	Dja	H3	Fl	Dr.Bhandari,PRL
Forest Vale	---	H4	Fl	Sydney
Pultusk	Pul	H5	Fl	Dr.Ray Davis
Allegan	Alleg	H5	Fl	Dr. Moore
Ambapur Nagla	AN	H5	Fl	G.S.I. 201
Beardslay	---	H5	Fl	Dr. Ray Davis
Ramsdorf	---	L	Fl	-do-
Saratov	Sar	L4	Fl	Dr.Krinov, # 317
Paragould	---	LL	Fl	Dr.Mason,NMNH,921
St. Mesmin	St.Mes	LL6	Fl	Dr.Pellas, # 368
Abee	---	E4	Fl	Dr.Moore, # 701
Atlanta	---	E6	Fd	-do-
Boreba	---	Euc.	Fl	Dr.Pellas, # 1297
Millibillille	---	Euc.		Dr.Binns,13198d
Sioux County	---	Euc.	Fl	Dr.Moore, # 198.3
Shalka	---	Dio.	Fl	G.S.I. 174.

Comparison with other groups is in reasonably good agreement. The higher values for Orgueil and Murray, reported by Injerd and Kaplan, 1974 may be due to sample heterogeneities, in view of the good agreement in the case of Murchison and Allende. The most serious disagreement seems to be the Abee value. In view of the large heterogeneities found in Abee meteorite (Kallemeyn et al., 1980) this discrepancy may not be real. Also, three clasts of Abee have variable mineral abundances (Rubin and Keil, 1980). The higher N value of ours for Abee fits the trend followed by other volatile elements, in being higher in Type I E-chondrites (Abee) compared to Type II E-chondrites (Atlanta) (Anders, 1964). Disagreement with the results from Chicago group exists in some cases, and is discussed in Chapter 2.

4.1.2 <u>Nitrogen in chondrules and lithic fragments</u> : A white inclusion in Allende has 12.9 ppm N compared to the bulk value of 44.5 ppm (Table 4.2). The white Allende inclusions (Ca-Al-rich inclusions) are the first solid objects to condense from the solar nebula around $\sim$ 1500°C (Grossman and Larimer, 1974) and N is not accreted at this high temperature and the prevailing oxygen fugacity. Chondrules in Saratov, Dhajala and Ambapur Nagla have lower N contents than the bulk. Also in Dhajala the light coloured chondrules have a N content of 7.6 ppm compared to 13.5 ppm in dark chondrules. Recent studies of chondrules from a number of meteorites

Table 4.2   Nitrogen (ppm) in various phases of meteorites
(nm = nonmagnetic, m = magnetic)

Meteorite	Phase	N(ppm) Replicate (Error= ±10%)	N(ppm) Mean	N_{nm}/N_m
Allende	Bulk	44.5	44.5	
	White Inc.	12.9	12.9	
Dhajala	Bulk	19.1,16.6,19.3	18.3	
	Dark Lithic Fragments	6.3	6.3	
	Dark Chondrules	13.5	13.5	
	Light Chondrules	7.6	7.6	
Forest Vale	Bulk	20.0,27.1	23.5	
Ambapur Nagla	Bulk	46.1,31.0,33.1	36.7	
	Chondrules	22.4	22.4	
	Pyroxene	21.1	21.1	
	Olivine	29.9	29.9	
	HCl Res.	196.4	196.4	
Saratov	Bulk	20.4,16.9,14.8	17.4	
	Chondrules	13.2	13.2	
St.Mesmin	Fusion Crust	16.0	16.0	
Beardslay	Bulk	35.0,32.4	33.7	
	m	28.7	28.7	
	nm	42.8	42.8	1.49
Abee	Bulk	505.7,495.5	500.6	
	m	478.2	478.2	
	nm	592.2	592.2	1.24
Atlanta	Bulk	108.2,85.3	96.7	
	m	57.4	57.4	
	nm	193.3	193.3	3.37

contd...

Table 4.2 (contd..)

Meteorite	Phase	N(ppm) Replicate (Error= ±10%)	N(ppm) Mean	N_{nm}/N_m
Bereba	Bulk	11.1,12.8	12.0	
Millibillille	Bulk	25.1,24.9	25.0	
Sioux County	Bulk	24.6,25.0	24.8	
Shalka	Bulk	15.0	15.0	
	Light grey matrix	15.3	15.3	
	Dark grey matrix	9.9	9.9	

Table 4.3   Comparison of N,Li in stone meteorites
with the literature data

Meteorite	N(ppm) This work	N(ppm) Literature	Li(ppm) This work	Li(ppm) Literature
Orgueil	834.9	3185[1],2400[1] 1476[2]	0.79	1.3 ± 0.1[13], 1.3[12],1.58[14]
Cold Bokkeveld	474.2	1300[1],563[3]	1.06	1.63[14]
Murray	528.3	1905[1],1018[2] 302[9]	1.26	1.12[10],1.6±0.2[13] 1.73[14]
Murchison	961.5	1975[1],845[2] 828[3],226[9]	1.62	1.71[14]
Allende	21.1 44.5	62[1],19[2],18[3] 15[9]	1.61 2.42	2.1±0.5[13],1.88[14]
Forest Vale	23.5	40[7]	2.28	1.71[13]
Saratov	17.4	42[7],104[7],27[8]	2.44	1.7±0.3[13]
St.Mesmin	16.0	77[7]		
Beardslay	33.7	59[7]	1.44	1.10[10]
Abee	500.6	277[3],270[4], 262[5]	1.20	1.31[10],2.88[11], 1.3[12],2.1±0.8[13], 2.28[15]

Table 4.3 (contd..)

Meteorite	N(ppm) This work	N(ppm) Literature	Li(ppm) This work	Li(ppm) Literature
Atlanta	96.7	247[5]	1.02	0.52 ± 0.08[13]
Bereba			9.01	9.94[15]
Sioux County	24.8	29[6]	9.65	8.87[15]
Pultusk			1.80	1.22[10]
Allegan			1.22	1.31[10], 1.21[13]

1. Gibson et al.,1971; 2. Injerd and Kaplan,1974; 3. Kung and Clayton,1978; 4. Moore and Gibson,1969; 5. Gibson et al.,1969; 6. Gibson et al.,1971; 7. Gibson and Moore,1971; 8.Vinogradov et al., 1963; 9. Müller,1974; 10. Quijano-Rico and Wänke,1969; 11, Shima and Honda,1966; 12. Krankowsky and Müller,1964; 13. Nichiporuk and Moore,1970; 14. Nichiporuk and Moore,1974; 15. Tera et al., 1970.

indicate that chondrules are formed by impact melting of chondritic masses ($\geq$ 10 cm in size) from which Fe-Ni-S separate out as an immiscible liquid and the remaining silicate-melt crystallises to give chondrules (Kerridge and Kieffer, 1977; Dodd, 1978a,b). This scenario can account for the texturally and chemically different chondrules in meteorites on the basis of sizes of the chondritic masses and the efficiency of Fe-Ni-S separation. Loss of N during this impact melting process could be responsible for the lower N content in chondrules.

Dark lithic fragments from Dhajala have 6.3 ppm N compared to bulk value of 18.3 ppm N. Ashworth and Barber, 1976 have attributed the lithification as due to passage of shock waves through porous aggregates of meteorites, causing deformation depending upon the intensity of shock. Lower N in Dhajala lithic fragments might be due to loss of N in the process of lithification.

4.1.3 <u>Nitrogen in magnetic and non-magnetic fractions</u> : N data on magnetic and non-magnetic portions is given in Table 4.2 and Table 4.4. The ratio N_{nm}/N_m is either close to unity (Allende, Dhajala, Forest Vale, Saratov and St.Mesmin) or greater than unity (Paragould, Pultusk, Ambapur Nagla, Beardslay, Abee and Atlanta). Abee and Atlanta have the mineral Osbernite (TiN) (Ramdohr, 1973). Its preferential enrichment in the non-magnetic portion might be the reason for higher N content in that portion.

In Ambapur Nagla, Olivine and Pyroxene were hand picked from 75-210 μm fraction, under a binacular microscope. N in these minerals is not enriched. It appears that N does not go with major minerals. Since no N bearing mineral has been identified in ordinary chondrites, the N enrichment might be due to the presence of a volatile rich component.

4.1.4 <u>Nitrogen in density separates</u> : The study of density separates was mainly intended for Li. But in the process we analysed N data also. Details of the separation of density fractions will be discussed in the section on Li. The N data on density fractions are given in Table 4.8. One important outcome of this study, is the high enrichment of N in the lightest separable phase (amounting to 0.24% in Ambapur Nagla, 0.18% in Allende and 3.0% in Forest Vale). Even more surprising is the fact that this same phase (from Allende and Ambapur Nagla) is enriched in Li also. It would be very interesting to characterize and study this phase for other elements. Admixture of this type of component would probably explain the enrichment of N and Li simultaneously in gas rich meteorites, as a carbonaceous phase of C1 or C2 type cannot account for Li enrichment.

4.1.5 <u>Nitrogen in sieve fractions</u> : The sieving is done after irradiation to avoid contamination problems. The irradiated meteorite piece is gently crushed to disaggregate the grains and sieved into various fractions. Each sieve size

fraction was separated into magnetic and non-magnetic portions using a hand-magnet. The process of crushing, if it is not gentle, will give size fractions which are not representative of the original meteorite sample and this can mask any grain size dependence. In the data presented in Table 4.5 for Bjurbole sieve fractions,one set shows a clear grain size dependence for N (from Shukla, 1977) while the second set shows uniform N (from Kothari, 1974). Kothari's data probably reflects homogeneisation during crushing. On the other hand, the grain size dependence, if present, cannot be an artifact of the crushing process. This has been shown to be the case by crushing further the > 270 μ fraction of Dhajala and separating into various size fractions. The data in Table 4.5 show the same N content for all the fractions. The low value of Li in > 75 μ fraction might be due to its higher metal content. But contrary to N, Li content depends on the mineralogy and mineralogical differences can account for different Li contents in sieve fractions. This is discussed in the Li section.

Further, it is possible that atmospheric nitrogen adsorbed on the meteorite surface prior to irradiation, inspite of best possible care taken in sample preparation, gives a fortutious surface correlated nitrogen. Our control experiments as discussed in the Experimental Chapter rule out such possibility. The above considerations gave us the

Table 4.4   Nitrogen (ppm) in various Sieve fractions of metearites; (N.Mag. = Non-magnetic, Mag. = Magnetic)

Size Fraction μ Meteorite	<38	38-75	75-151	151-270	>270	Bulk*	N_{nm}/N_m
Orgueil All Mag.	785.8	835.7	839.4	856.9	854.7	843.9	
Cold Bokkeveld All N.Mag	454.2	455.3	457.5	492.4	473.6	474.2	
Murray All N.Mag.	494.7	544.3	569.4	–	–	528.3	
Murchison All N.Mag.	783.4	952.6	1126.3	1009.3	–	961.5	
Allende Mag.	–	53.8	26.0	20.7	19.8	20.5	
Allende N.Mag.	23.1	15.3	13.0	13.0	19.5	18.0	0.88
Fayetteville Mag.	–	–	–	26.8	–		
Fayetteville N.Mag.	36.3	29.3	26.6	21.9	–		
Dhajala Mag.	–	–	14.1	21.0	13.2	17.1	
Dhajala N.Mag.	21.4	21.2	18.9	13.7	13.3	16.4	0.96
Forest Vale Mag.	–	40.8	20.9	23.8	21.9	22.7	1.07
Forest Vale N.Mag.	82.2	36.1	34.6	23.7	15.8	24.4	
Pultusk Mag.	–	60.0	55.4	33.5	24.0	26.0	
Pultusk N.Mag.	37.5	38.0	39.7	29.2	28.3	34.5	1.33

Table 4.4 (contd..)

Size Fraction μ / Meteorite	<38	38-75	75-151	151-270	>270	Bulk[*]	N_{nm}/N_m
Ambapur Nagla Set 1 : Mag.	145.0	898.6	80.6	57.8	22.9	36.5	1.25
N.Mag.	194.5	137.1	73.4	36.5	22.2	45.8	
Ambapur Nagla Set 2 : Mag.	990.0	128.9	83.3	41.9	21.2	34.7	
N.Mag.	147.8	100.6	53.7	29.6	23.7	39.9	1.15
Ambapur Nagla Set 3 : Mag.	758.0	-	-	-	-	-	-
N.Mag.	233.4	-	-	-	-	-	
Saratov Mag.	-	21.5	20.6	19.2	18.2	18.6	
N.Mag.	22.7	24.3	23.0	18.6	10.1	15.5	0.83
Paragould Mag.	-	n.d	4.6	12.1	7.7	8.1	1.15
N.Mag.	15.8	21.3	8.4	8.2	8.5	9.3	
St.Mesmin Mag.	-	29.3	19.8	19.3	-	20.3	
N.Mag.	21.6	21.8	19.3	26.3	-	21.0	1.03
Shalka All N.Mag.	21.2	23.7	21.8	8.2	16.0	14.9	

[*]Computed.

Table 4.5 N and Li in Dhajala and Bjurbole to
show the affect of sieving procedure

Sample	N (ppm)	Li (ppm)
Dhajala >270 μ* (Homogenized)	23.8	1.52
<38μ from *	21.7	1.76
38-75μ -do-	22.4	1.58
>75μ -do-	21.4	0.58
Bjurbole	Set 1[a]	Set 2[b]
<38μ	65	38
38-75	44	29
75-151	41	33
151-270	44	33
>270	34	34

a. From Shukla, 1977; b. From Kothari, 1974.

confidence that the sieve analysis results of N are not
artifacts and represent the nitrogen distribution in meteori-
tes. The results on each group of meteorites will be dis-
cussed separately.

Carbonaceous Chondrites : Our Orgueil sample has no non-
magnetic portion whereas the Murray, Murchison and Cold
Bokkeveld samples are completely non-magnetic. The N data
for size fractions are shown in Table 4.4 and represented
in Fig. 4.1 on N vs m.g.d. (mean grain diameter), plots. As
can be seen N is independent of grain size in Orgueil and
Cold Bokkeveld, whereas N increases as grain size increases
in Murray and Murchison, the trend being much pronounced for
Murchison. Co and Eu have also been analysed in these
fractions. The results are shown in Table 4.6 for Co and
Table 4.7 for Eu and plotted against m.g.d. in Fig. 4.2 for
Co and Fig. 4.3 for Eu. For Cold Bokkeveld N is independent
of grain size unlike Co and Eu,both of which vary in a
similar fashion. In Orgueil also N is independent of grain
size while Co and Eu decrease with increasing grain size.
Co has a tendency to get concentrated in Kamacite (Rambaldi,
1976) while REE are enriched in phosphate minerals (Rambaldi
and Fredriksson, 1977). Variations of Co and Eu reflect the
differences in mineral compositions of the grain size fractions.
The independent behaviour of N reflects the fact that N is
independent of mineralogy in these two meteorites. But in
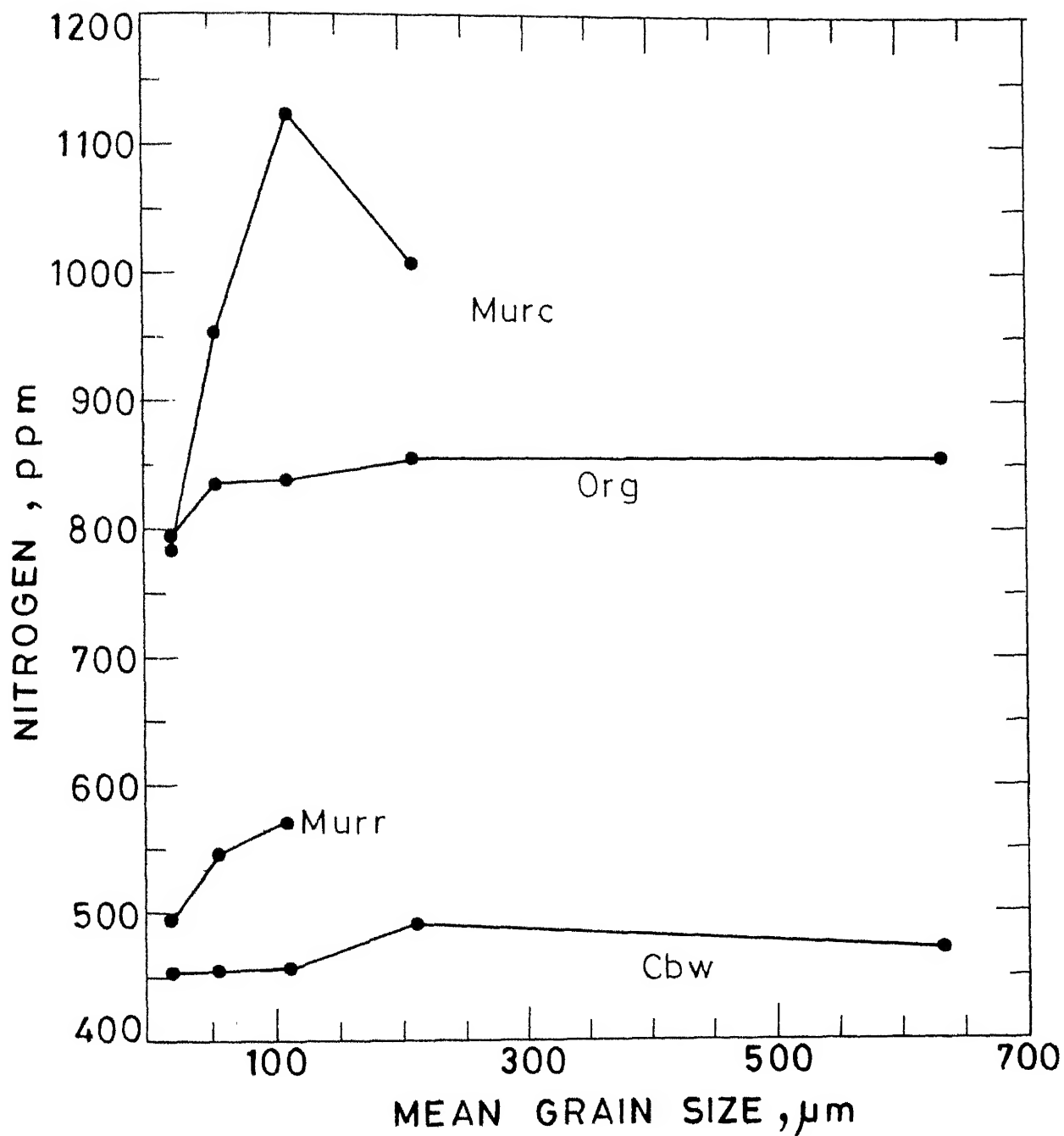
Fig. 4.1   N vs. mean grain size for carbonaceous chondrites.

Table 4.6   Cobalt (ppm) in various sieve fractions
of meteorites(error = ± 2 percent)

Size fraction μ Meteorite	<38	38-75	75-151	151-270	>270	Bulk	Bulk Lit.
Orgueil All Mag.	699.9	552.0	485.6	466.4	424.9	496.4	524[1]
Cold Bokkeveld All N.Mag.	809.9	341.7	533.0	966.3	455.0	713.4	
Murray All N.Mag.	552.2	320.5	320.7	–	–	431.6	592[1]
Murchison All N.Mag.	473.6	498.8	547.6	526.2	–	509.9	
Fayetteville Mag.	473.0	737.7	1527.0	1891.3	–	1493.0	
N.Mag.	61.2	56.0	86.7	73.6	–	68.0	
Allegan Mag.	–	–	128.2	177.0	–	–	
N.Mag.	52.0	136.5	129.8	47.2	43.2	76.3	
Paragould* Mag.	–	5.1	1.6	2.1	1.8	2.0	
N.Mag.	1.0	0.2	0.16	0.21	0.31	0.29	

*These values are relative to Co = 1 in $<38μ$.N.Mag.

1. Nichiporuk et al., 1967.

Table 4.7 Europium (ppb) in various sieve fractions of meteorites; (Error = ± 5 percent) (N.Mag. = Non-magnetic; Mag. = Magnetic)

Size fraction μ Meteorite	< 38	38-75	75-151	151-270	>270	Bulk	Bulk Lit.
Orgueil All Mag.	123.0	88.0	66.9	49.8	56.6	65.5	54.0[1]
Cold Bokkeveld All N.Mag.	173.0	50.3	121.0	153.0	77.0	125.4	
Murray All N.Mag.	78.7	52.3	56.7	–	–	66.3	73.0[1]
Murchison All N.Mag.	60.8	79.6	109.0	69.0	–	80.3	79.0[1]
Fayetteville Mag.	n.d	n.d	n.d	n.d	–	–	
N.Mag.	66.8	78.3	91.9	70.7	–	77.0	
Allegan Mag.	–	–	79.3	111.0	–	–	
N.Mag.	104.0	323.0	505.0	127.0	70.6	204.4	
Paragould* Mag.	–	1.42	0.33	0.29	0.38	0.36	
N.Mag.	1.0	0.36	0.32	0.34	0.35	0.36	

n.d. = Not detected.

* These values are relative to Eu = 1 in < 38 μ N.Mag.

1. Knab and Hintenberger, 1979.

Table 4.8 Nitrogen in various density fractions of
meteorites (ppm)

Meteorite \ Density Fraction g/cc	<2.55	>2.55 <2.97	>2.97	Bulk*
Allende	–	423.2	44.3	45.0
HCl Residue	33.3	33.8	83.0	35.9
Forest Vale	–	107.2	12.6	15.5
HCl Residue	–	18.9	20.0	19.5
Ambapur Nagla	–	124.5	18.5	18.7
HCl Residue	–	16.9	25.5	21.3
Abee	–	501.4	439.6	445.0
HCl Residue	–	466.5	486.0	484.1
Boreba	95.6	22.6	16.7	18.5
HCl Residue	–	13.1	18.3	16.8
Millibillillo	16.8	25.0	25.4	25.0
HCl Residue	–	20.6	19.0	19.5
Sioux County	–	16.4	18.3	17.7
HCl Residue	–	18.6	14.7	15.5
Shalka	–	–	7.7	7.7
HCl Residue	–	–	9.1	9.1

*Computed.
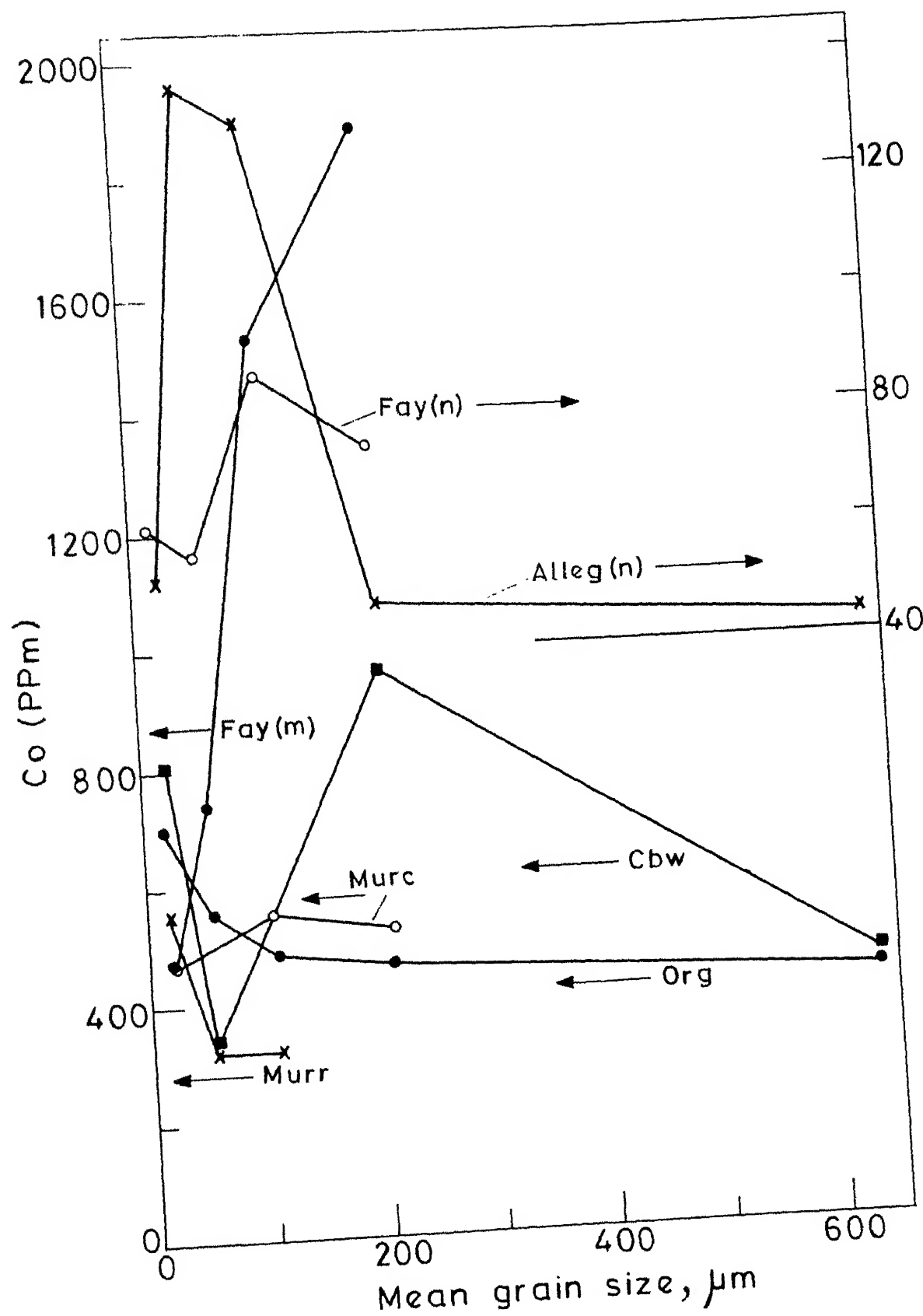
Fig. 4.2 Co vs. mean grain diameter for various meteorites.
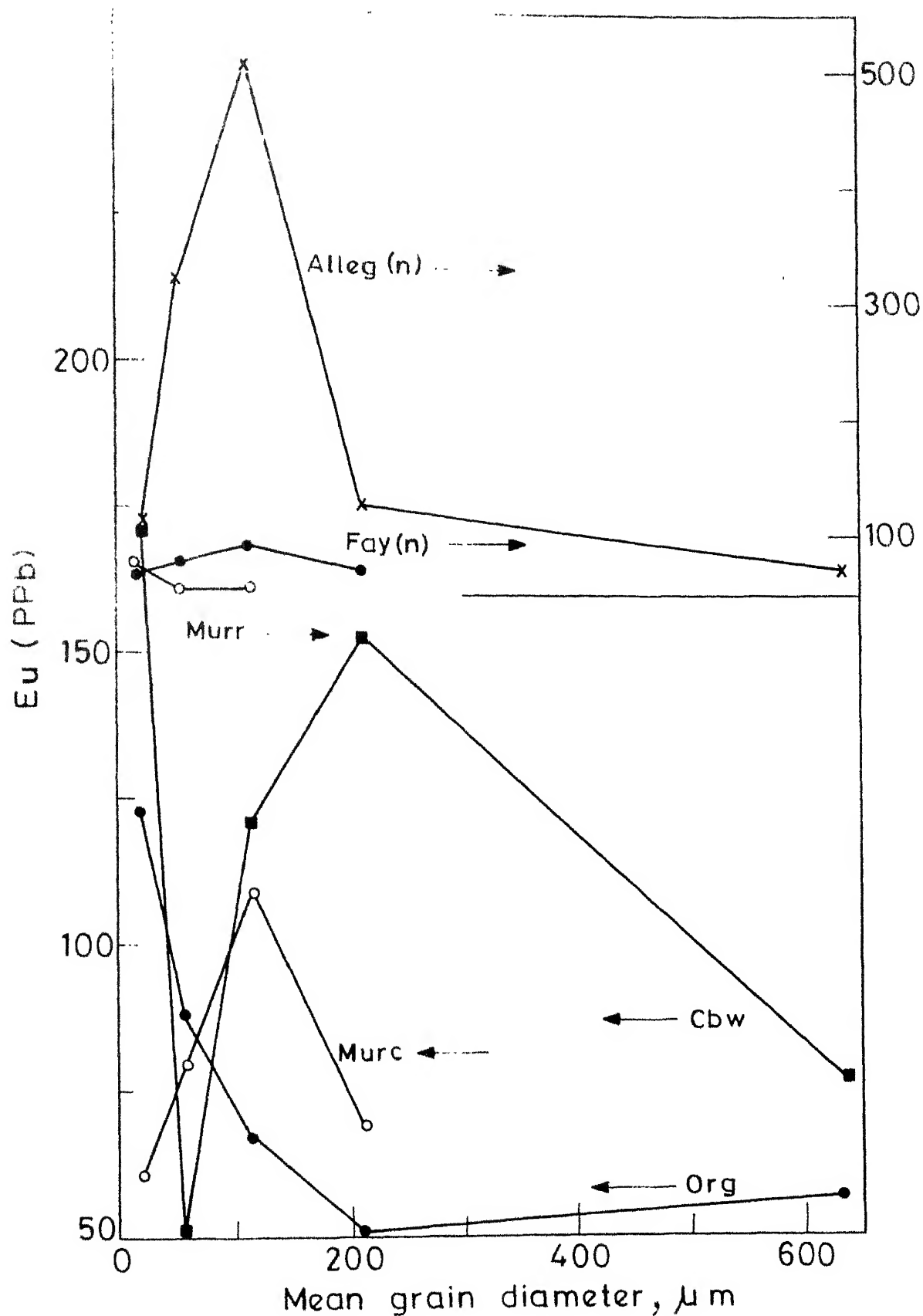
Fig. 4.3 Eu vs. mean grain diameter for various meteorites.

Murray, Co and Eu decrease while N increases with increasing grain size while in Murchison all three elements Co, Eu and N co-vary increasing with increased grain size. Here again mineralogical differences are reflected by Co and Eu variations but the non-parallel variation of N in Murray and a co-variation of N in Murchison again points out that N variation is not a mineralogical consequence.

Ordinary Chondrites : Nitrogen in Allende is similar in amount, to ordinary chondrites. Hence, it is grouped with other ordinary chondrites for discussion. Including Allende and the achondrite Shalka, we have studied ten meteorites comprising H group (5), L (1) and LL (2), for nitrogen in grain size separates of magnetic and non-magnetic portions. The results are shown in Table 4.4.

Shalka has no magnetic portion. The non-magnetic portion does not show any grain size dependence. The meteorites Forest Vale, Allegan, and Paragould have been shown to have carbon enrichment in the fine grain fractions (Noonan et al., 1972; Fredriksson and Nelson, 1969). These meteorites will be henceforth referred as 'carbon-rich meteorites'. The 'elusive matrix' in these meteorites has also been enriched in Zn and Pb (Fredriksson, 1973, private communication). Another meteorite belonging to this group, Bjurbole, has been shown to have similar enrichment of N (Shukla, 1977).

Forest Vale non-magnetic portion shows a clear cut grain size dependence for N, similar to C. Paragould has a very irregular trend for N, both in magnetic and non-magnetic portions. Co and Eu for Paragould show a high value in the fine grain size for both magnetic and non-magnetic fractions and have a constant value in the rest of the size fractions. Paragould is a highly shocked and brecciated meteorite (Chou and Cohen, 1973; Fredriksson et al., 1968) and as such will not be taken seriously for drawing any conclusions.

In all the meteorites studied, the finest fraction always has higher N content compared to the coarsest fraction. But a gradual decrease with increasing grain size is not evident in some cases, probably due to the fact that during crushing, some coarse grains got crushed and contaminated the fine fraction, thus masking the effect. The magnetic portions of Allende, Pultusk, Ambapur Nagla and St. Mesmin and the non-magnetic portions of Fayetteville, Forest Vale and Ambapur Nagla show the grain size dependence for nitrogen. The N vs.m.g.d. plots for Pultusk, Allende, St. Mesmin and Fayetteville are given in Fig. 4.4, and for Dhajala, Saratov and St. Mesmin are given in Fig. 4.5. For Forest Vale and Ambapur Nagla the N data are plotted against 1/r in Fig. 4.6 where the lunar soil 14163 is also given for comparison (Data for 14163 are from Kothari, 1974).
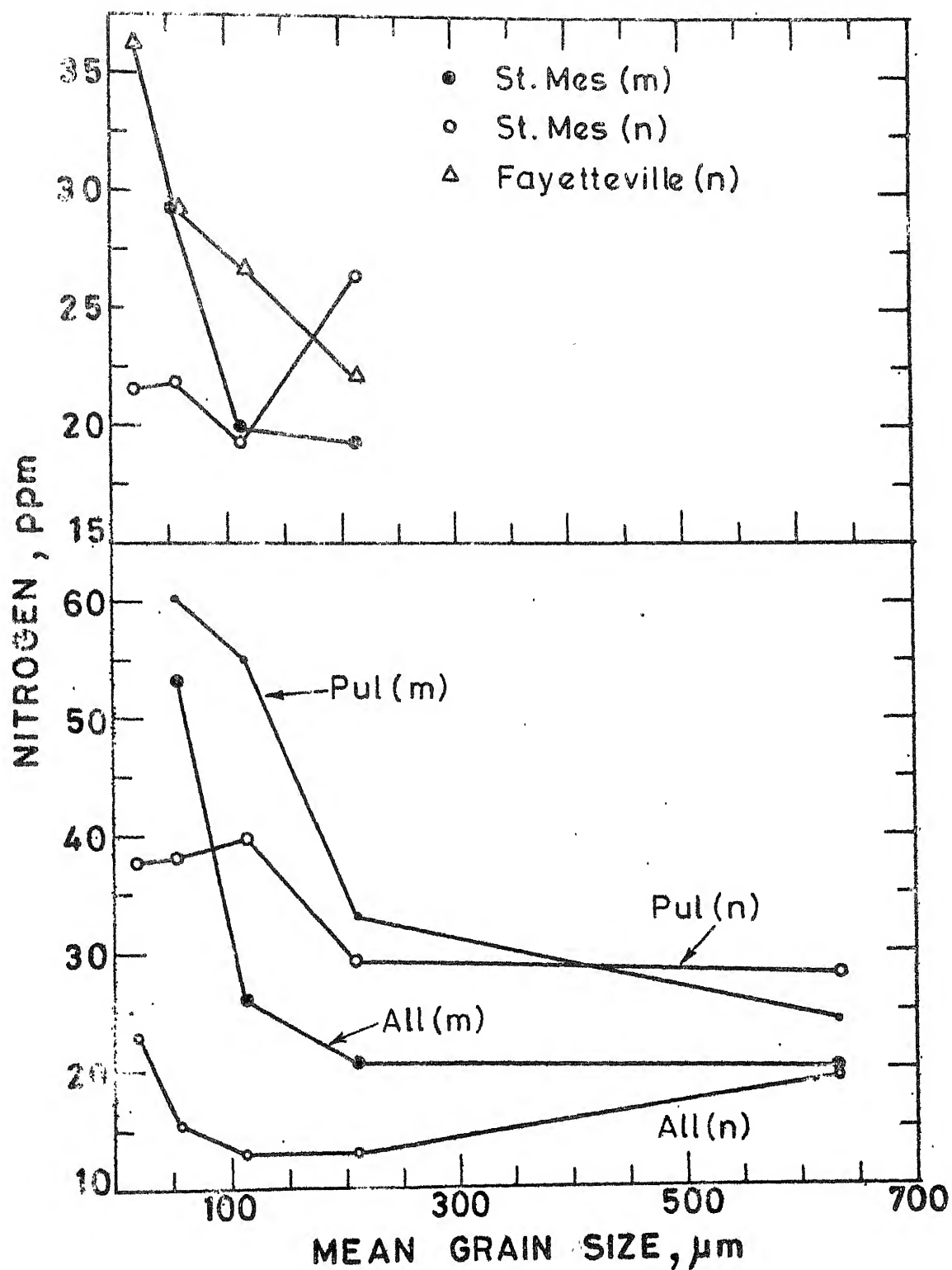
Fig. 4.4 N vs. mean grain diameter for Allende and gas-rich meteorites.
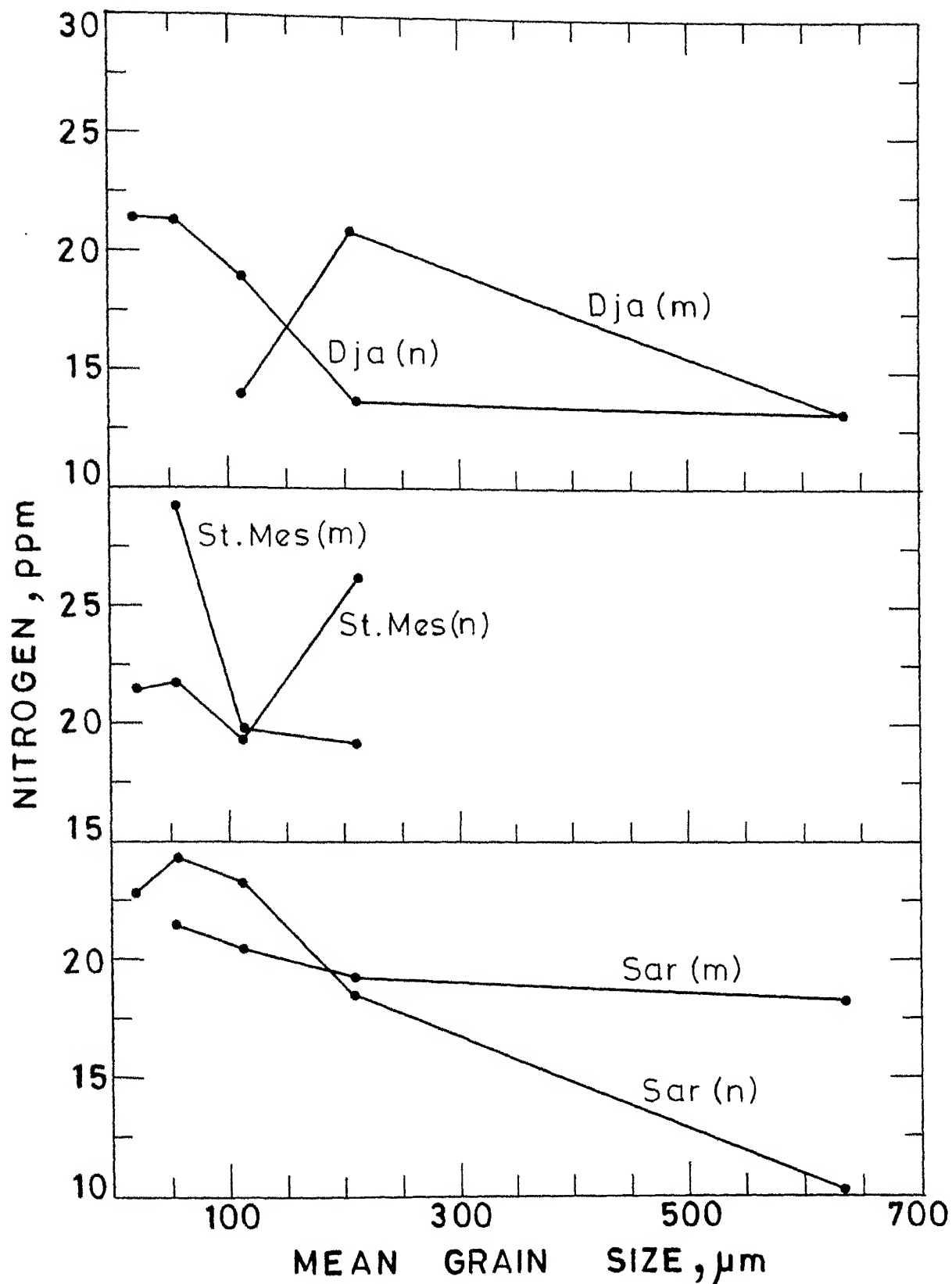
Fig. 4.5 N vs. mean grain diameter for Dhajala, Saratov and St. Mesmin.

In case of Fayetteville Co and Eu are also analysed (Table 4.6 and Table 4.7) which are shown in Fig. 4.2 and Fig. 4.3 respectively. Both Co and Eu show non-parallel trends with respect to each other and also with respect to nitrogen. This reflects the different mineralogy of the various size fractions and also that N variation may not be due to mineralogical differences. Fayetteville, St. Mesmin and Pultusk are polymict brecciated gas rich meteorites. They contain solar wind noble gases (Schultz and Signer, 1977) and solar flare tracks (Bhattacharya et al., 1975; Ducatel and Poupeau, 1974) and as such should have solar wind nitrogen also. But calculations based on solar wind noble gas amounts have revealed that only a maximum of ~ 1 ppm N of solar wind origin can be present in gas-rich meteorites (Kung and Clayton, 1978). Nearly ubiquitous C-enrichments in gas-rich meteorites (Begemann and Heinzinger, 1969) and very scattered data for a few volatile elements, led Suess et al., 1964, Müller and Zähringer, 1966 and Mazor and Anders, 1967 to suggest that the dark material in gas rich meteorites to be carbonaceous like. This may be true for gas-rich achondrites only, but not for gas-rich chondrites, as shown by the study of volatile elements in dark and light portions of these meteorites (Bart and Lipschutz, 1979). These authors have suggested that both light and dark portions of each chondrite represent a 'compositionally more extended' sampling of parental nebular material, hitherto unknown. More recently,

McSween Jr. and Lipschutz, 1980 have suggested that in the case of brecciated H chondrites atleast, the volatile enrichment in the dark portions is due to admixture of unequilibrated material of the same class with equilibrated material similar to that in the light portions. Nitrogen or lithium enrichments cannot be accounted for by the admixture of unequilibrated material as the U.O.C. Dhajala (H3) does not show enrichment of N or Li. The N and Li enrichments might be due to presence 'compositionally more extended' material. This material might be similar to the light density fraction of Allende which is simultaneously enriched in N and Li and may probably be enriched in other volatiles as well.

Ambapur Nagla and Forest Vale are unlike the rest of the meteorites. Forest Vale has C (Noonan et al., 1972) Zn and Pb (Fredriksson, 1973) enrichments in fine grain fractions. Our N and Li data for the Forest Vale sample have been reduced to the grain sizes for which C data was available and C vs N (Fig. 4.7) and C vs Li (Fig. 4.8) have been plotted. Inspite of the fact that C data and N and Li data were on different pieces, a very good correlation is obtained. Similar behaviour has been observed in the case of Bjurbole meteorite. N, Li data were extracted from Shukla, 1977 and C data from Fredriksson and Nelson, 1969. A trend (C vs. N and C vs. Li) similar to that of Forest Vale was noted. The implications will be discussed towards the end of this chapter.
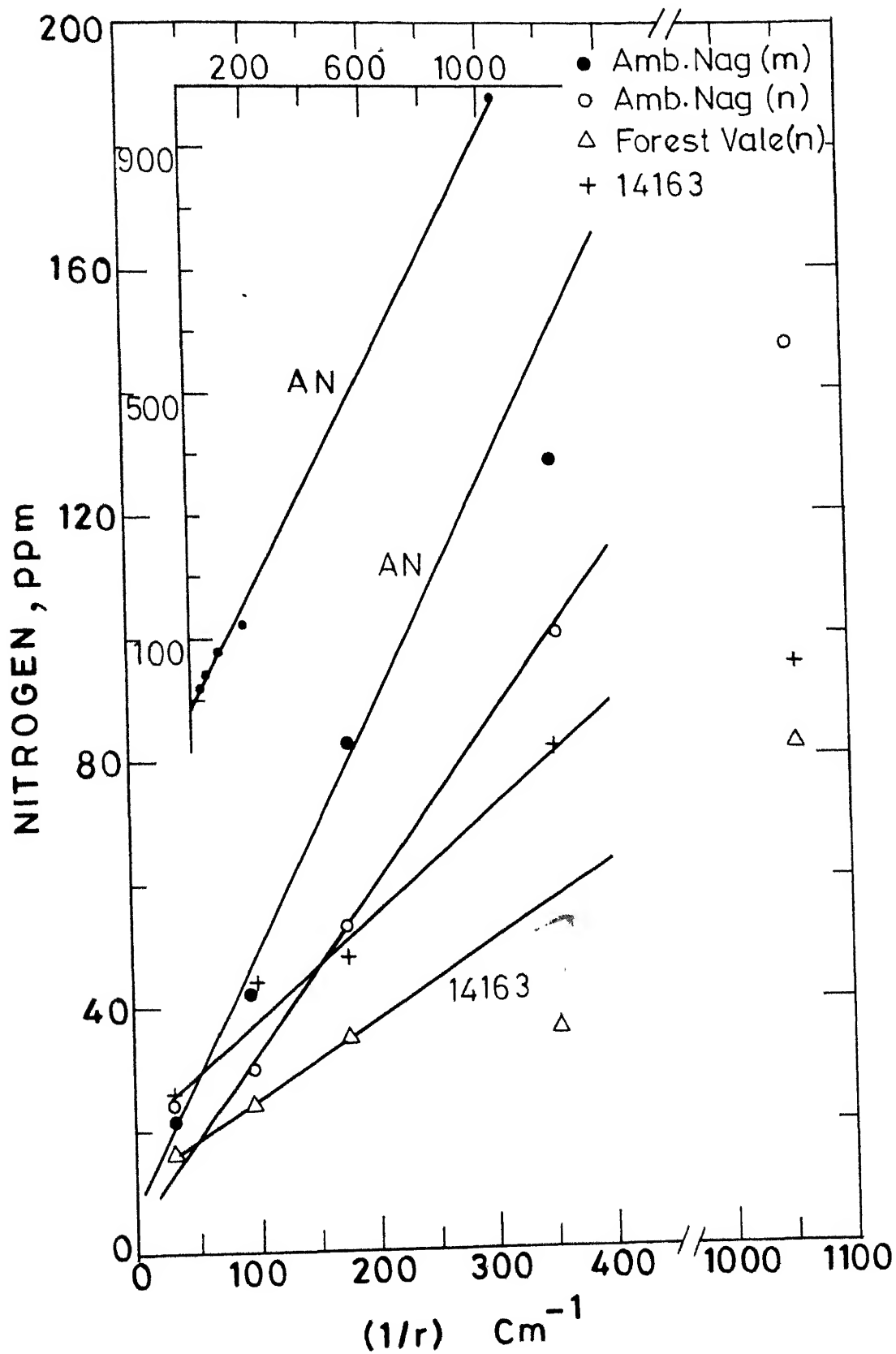
Fig. 4.6 N vs. $\frac{1}{r}$ for Forest vale, Amb. Nagla and 14163.
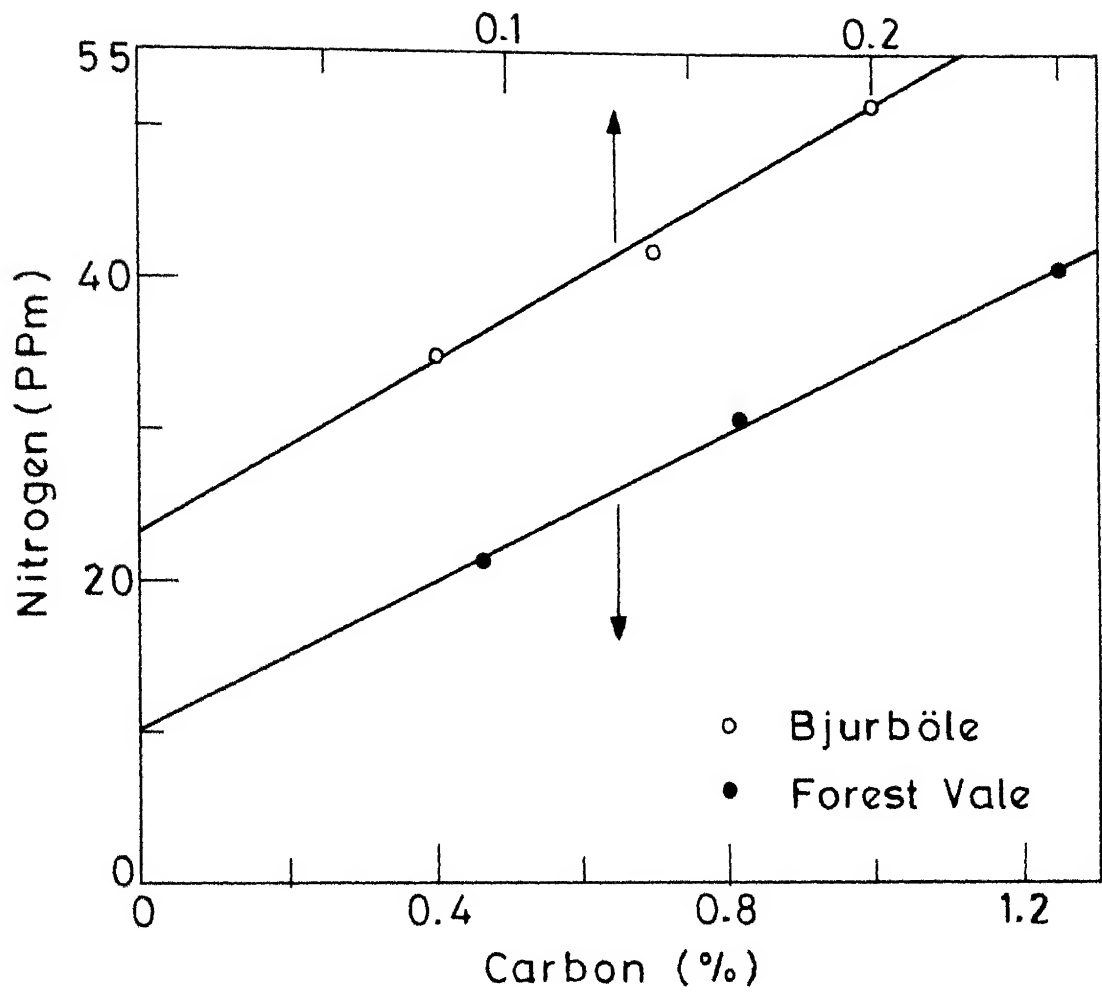
Fig.4.7   C   vs. N for carbon-rich meteorites.
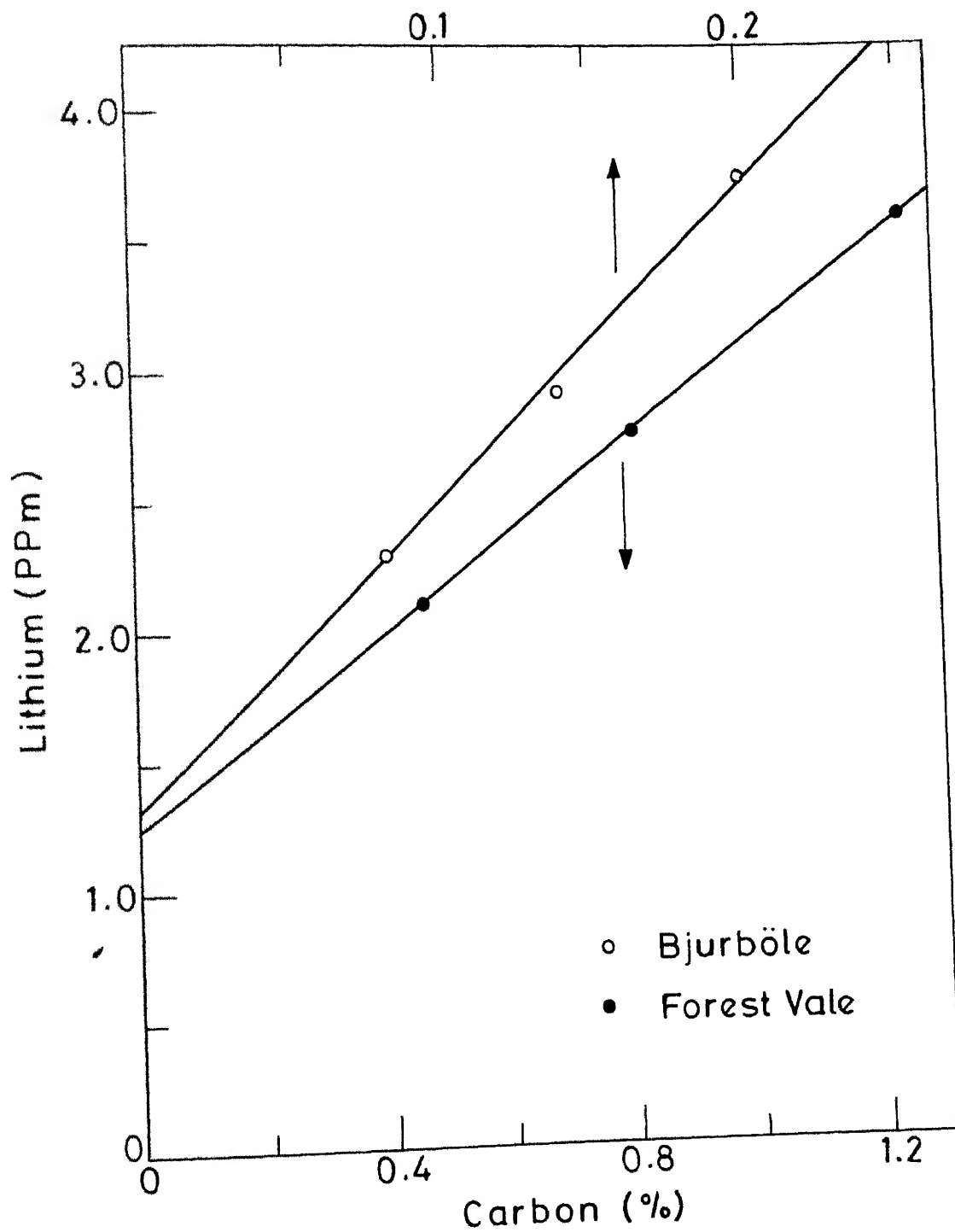
Fig.4.8 C vs. Li for carbon-rich meteorites.

Recently Ambapur Nagla has been thoroughly studied by a consortium group. The petrological studies have shown that Ambapur Nagla has shock effected orthopyroxenes (Ashworth, 1980) shock mobilised troilite (Hutchison et al., 1980) and corroded silicate (Christophe-Michel-Levy, 1981) and a metal phase indicative of reheating followed by rapid cooling through about $500^{\circ}C$ (Hutchison et al., 1980). A relation between corrosion of silicates and mobilisation of sulphide may exist if H_2SO_4 or H_2S has been produced during the late heating event (Christophe-Michel-Levy, 1981) which occurred, as shown by the loss of radiogenic and spallogenic rare-gases (Pellas et al., 1979; Zähringer, 1968). There was no anomaly in trace element chemistry, (Hertogen et al.,1978) N and Li (this work) and B content (Curtis et al., 1980) in the bulk meteorite.

The plot of N vs.$1/r$ for both Ambapur Nagla magnetic and non-magnetic fractions and Forest Vale non-magnetic together with 14163 are shown in Fig. 4.6. They are all similar. 14163 has mainly solar wind nitrogen. The leaching of $< 38 \mu$ mag. portion of Ambapur Nagla with 1.5 percent HNO_3 does not remove any N (Table 2.3, Chapter 2) clearly indicating that N was not surface correlated. Due to the very small amount of sample (< 1 mg) it could not be characterized with the facilities at our disposal. The magnetic portion of Ambapur Nagla shows a similar high enrichment for

Li also,whereas Li is uniform in all size fractions of non-magnetic fraction. We call the fine grained magnetic fraction of Ambapur Nagla 'Peculiar' because of these peculiar features. Its implications will be discussed in the end.

4.2 Lithium in Meteorites

4.2.1 Lithium in bulk meteorites : Our Li data on bulk meteorites are presented in Table 4.9 and Table 4.10 and a comparison of our data with the literature data is given in Table 4.3. There is a very good agreement of our data with the literature data. But there are two notable exceptions. Our Orgueil value of 0.79 is roughly half of the literature value (1.58) and the Atlanta value of ours is twice as much compared to the reported value of 0.52 ppm. These differences could be due to sampling problems.

Eucrites have the highest Li content among stone meteorites. Terrestrial basalts (BCR-1) and lunar basalts (Shukla, 1977) have a similar high Li content. Moon, earth and Eucrites have many features common to them (Anders, 1977).

4.2.2 Lithium in chondrules and lithic fragments : A white inclusion from Allende has 1.3 ppm Li, which is not much different from the bulk Li content. Taking the view that Li may not be refractory in nature (Dreibus et al., 1976; Hutcheon et al., 1977; Phinney et al., 1979) the normal Li content of this white inclusion might be due to the presence

Table 4.9   Lithium (ppm) in various phases of
            meteorites
            (nm = non-magnetic, m = magnetic)

Meteorite	Phase	Li		Li_{nm}/Li_m
		Replicate (error=±10%)	Mean	
Allende	Bulk	2.42	2.42	
	White Inc.	1.34	1.34	
Dhajala	Bulk	1.47,1.65,1.95, 1.68,1.65,1.25, 1.77,1.87	1.66	
	Dark Lithic Frag.	0.19	0.19	
	Dark Chond.	0.89	0.89	•
	Light Chond.	0.93	0.93	
Forest Vale	Bulk	2.32,2.24	2.28	
Ambapur Nagla	Bulk	1.62,1.60,2.71,	1.98	
	Chond.	0.92	0.92	
	Pyroxone	1.60	1.60	
	Olivine	4.26	4.26	
	HCl Res.	1.12	1.12	
Beardslay	Bulk	1.27,1.61	1.44	
	m	1.09	1.09	
	nm	1.72	1.72	1.58
Ramsdorf	Bulk	1.95	1.95	
Saratov	Bulk	2.23,3.16,1.92,	2.44	
	Chond.	1.42	1.42	
St.Mesmin	Fusion Crust	2.80	2.80	
Abee	Bulk	1.07,1.32	1.20	
	m	1.05	1.05	
	nm	1.49	1.49	1.42
Atlanta	Bulk	1.00,1.04	1.02	
	nm	1.46	1.46	

Table 4.9 (contd..)

| Meteorite | Phase | Li | | Li_{nm}/Li_m |
		Replicat. (error=±10%)	Mean	
Beroba	Bulk	8.57,9.46	9.01	
Millibillillo	Bulk	8.43,9.00	8.71	
Sioux County	Bulk	9.73,9.57	9.65	
Shalka	Bulk	1.07	1.07	
	Light grey matrix	0.85	0.85	
	Dark grey matrix	0.89	0.89	
	Pyroxene	2.36	2.36	
	Olivine	2.06	2.06	
	Ilmenite	1.09	1.09	
	HCl Res.	1.12	1.12	

Table 4.10 Lithium (ppm) in various sieve fractions
of meteorites
(N.Mag. = Non-magnetic; Mag. = Magnetic)

Size fraction μ / Meteorite	<38	38-75	75-151	151-270	>270	Bulk*	Li_{nm}/Li_m
Orgueil All Mag.	0.80	0.87	0.81	0.73	0.86	0.79	
Cold Bokkeveld All N.Mag.	1.09	1.02	1.03	1.08	1.11	1.06	
Murray All N.Mag.	1.33	1.31	1.13	-	-	1.26	
Murchison All N.Mag.	1.68	1.73	1.55	1.51	-	1.62	
Allende Mag.	-	1.42	1.90	1.70	1.50	1.57	
N.Mag.	1.54	1.51	1.51	1.79	1.76	1.66	1.06
Fayetteville Mag.	1.13	2.24	1.82	1.01	-	1.37	
N.Mag.	2.54	2.41	2.23	1.90	-	2.34	1.71
Dhajala Mag.	-	-	1.21	1.26	0.81	1.08	
N.Mag.	2.16	2.13	2.32	1.75	1.15	1.81	1.67
Forest Vale Mag.	-	1.80	1.05	1.29	1.38	1.33	
N.Mag.	4.16	3.73	3.18	2.93	2.48	2.89	2.17
Pultusk Mag.	-	1.20	1.95	1.50	1.30	1.33	
N.Mag.	2.35	2.15	2.20	2.38	1.89	2.20	1.65
Allegan Mag.	-	-	2.90	2.59	0.51	0.57	
N.Mag.	2.82	2.96	3.10	2.86	2.56	2.83	4.96

Table 4.10 (contd...)

Size fraction μ / Meteorite		<38	38-75	75-151	151-270	>270	Bulk*	Li_{nm}/Li_m
Ambapur Nagla								
Set 1	Mag.	164.2	16.0	4.01	2.44	1.40	2.15	
	N.Mag.	3.01	2.95	2.73	2.58	2.11	2.34	1.09
Set 2	Mag.	41.0	6.06	1.80	2.14	1.08	1.54	
	N.Mag.	1.91	2.49	1.97	1.82	1.43	1.66	1.08
Set 3	Mag.	5.85	-	-	-	-	-	
	N.Mag.	5.14	-	-	-	-	-	
Saratov								
	Mag.	-	1.23	1.94	2.19	1.62	1.75	
	N.Mag.	2.58	3.20	2.60	2.42	1.86	2.24	1.28
Paragould								
	Mag.	-	3.60	3.00	3.03	2.85	2.95	
	N.Mag.	2.75	2.90	3.02	2.97	3.19	2.99	1.01
St.Mesmin								
	Mag.	-	1.23	1.26	1.81	-	1.64	
	N.Mag.	2.70	2.66	2.60	2.04	-	2.62	1.60
Shalka								
All	N.Mag.	0.72	0.88	0.84	0.98	1.21	0.99	

*Computed.

of a minor Li carrying phase. Dark lithic fragments of
Dhajala have very low Li content (0.19 ppm) compared to the
value of 1.7 ppm for the bulk meteorite. Chondrules from
Dhajala, Saratov and Ambapur Nagla all have lower Li compared
to the matrix. Shukla, 1977 has reported higher Li also in
chondrules of some meteorites. The recent physical (Hughes,
1980) chemical (Fredriksson et al., 1978) and petrological
studies (Grossman J.N. et al., 1978; Lux et al., 1980) have
revealed differences in the compositions of individual chon-
drules from the same meteorite as well as between chondrules
belonging to meteorites of different petrological types.
Such differences might also be present for Li.

4.2.3 Lithium in separated minerals : Hand picked minerals
from Ambapur Nagla and Shalka have been studied for Li. In
Ambapur Nagla Olivine has a higher Li content than pyroxene
by a factor of $\sim$ 2.5. Also the HCl insoluble portion of the
meteorite has 1.1 ppm Li compared to bulk value of 2.0 ppm Li.
These finding are in agreement with the suggestion of Shima and
Honda,1967b that Li is enriched in a HCl soluble phase which
is probably olivine. But this may be true only for chondrites.
For the differentiated achondrites the situation may be
different.

In Shalka meteorite, the olivine and pyroxene have Li
contents which are a factor of 2 higher than the bulk value,
while ilmenite has Li similar to the bulk Li content. Also the

HCl residue has the same value as the bulk meteorite.

4.2.4 <u>Lithium in density separates</u> : To further understand the behaviour of Li in meteorites, we analysed various density separates. Although the hand-picked minerals give pure samples, it is often laborious and requires about 1 gm. meteorite sample to get 1 mg pure mineral grains. The density fractions give a mineral concentrate only, but have the advantage of small sample requirement, and can be carried out after irradiation, thus avoiding any contamination problems.

In Table 4.11 the specific gravities of the important meteoritic minerals and their susceptibility to HCl are given. In the same table the sp. gr. of some liquids used for density separations have been given. We have used 1,1,2,2,tetrabromoethane (ρ = 2.97 g/cc) and a mixture of (21:79) methanol and tetrabromoethane which gives ρ = 2.55 g/cc. With these two liquids we separated the three fractions with densities $\rho <$ 2.55; 2.55 $< \rho <$ 2.97 and 2.97 $< \rho$. The meteorite piece was ground to a powdery mass and first centrifuged with the heavier liquid (ρ = 2.97 g/cc) till a clear separation was achieved. The mass settled at the bottom of the centrifuge tube was separated by suctioning into a dropper. Both the fractions were thoroughly washed with ether to completely remove tetrabromoethane and dried. Then the $\rho <$ 2.97 fraction was again centrifuged with the lighter liquid (ρ = 2.55 g/cc) and the two density fractions were separated,

cleaned and dried as above. In case of chondrites the fraction $\rho < 2.97$ was so small, that we did not separate it further, while the meteorites Shalka, Sioux County and Abee have no fraction with density $\rho < 2.55$ g/cc. From the Table 4.11, it can be seen that our $\rho < 2.55$ fraction can have graphite and other lighter components like carbonaceous material, the fraction $2.55 < \rho < 2.97$ can have mainly plagioclase and the rest in $\rho > 2.97$ (mostly Olivine and Pyroxene + metal and troilite).

In order to get rid of most of the minerals and get much better mineral concentrates we treated the meteorite powder with 6N HCl for 2 days. This treatment removes Fe-Ni, CaS, Ca-PO$_4$, Troilite and Olivine completely. The HCl residue was washed and dried and separated into lighter and heavy fractions using tetrabromoethane (Shima and Honda, 1967a,b). The 2.55 g/cc liquid did not give a lighter fraction in the residue except in the case of Allende. The fraction $\rho < 2.97$ in the residue corresponds to nearly pure plagioclase and the $\rho > 2.97$ fraction approximates to a good pyroxene sample.

The Li results for density separates of bulk meteorite as well as for HCl residue are given in Table 4.12. The meteorites studied include one carbonaceous chondrite (Allende) one E-chondrite (Abee) two H-chondrites (Forest Vale and Ambapur Nagla) and four achondrites (Shalka (diogenite) Bereba, Sioux County and Millibillillie (Eucrites)).

Table 4.11   Specific gravities of meteoritic
minerals and some useful liquids

Mineral/ Liquid	Specific gravity	Susceptibility to HCl
Graphite	2.23	Resistant
Oldhamite	2.58	Decomposes
Plagioclase	2.62 - 2.76	Resistant
Pyroxene	3.1 - 3.5	Resistant
Olivine	3.27 - 4.27	Dissolves
Enstatite	3.2 - 3.5	Dissolves
Chromite	4.6	Resistant
Ilmenite	4.7	Dissolves
Troilite	4.7	Decomposes
Magnetite	5.18	Dissolves
Kamacite	7.3 - 7.9	Dissolves
Taenite	7.8 - 8.2	Dissolves slowly
Liquids		
Methanol	0.789	
Ethanol	0.795	
Bromoform	2.89	
1,1,2,2-Tetra Bromoethane	2.97	
Methylene Iodide	3.32	

Table 4.12   Lithium (ppm) in various density
fractions of meteorites

Density Fraction g/cc. / Meteorite	<2.55	>2.55 <2.97	>2.97	Bulk*
Allende	--	11.47	2.48	2.50
HCl Residue	0.84	2.70	2.52	1.10
Forest Vale	--	1.88	2.21	2.20
HCl Residue	--	2.30	1.06	1.61
Ambapur Nagla	--	7.28	1.38	1.40
HCl Residue	--	1.39	0.87	1.12
Abee	--	1.45	1.00	1.04
HCl Residue	--	1.95	1.65	1.68
Bereba	9.50	16.33	11.00	12.30
HCl Residue	--	7.30	8.35	8.04
Millibillille	6.63	12.38	9.80	10.20
HCl Residue	--	7.79	7.77	7.78
Sioux County	--	13.92	9.81	11.18
HCl Residue	--	8.56	7.88	8.02
Shalka	--	--	1.29	1.29
HCl Residue	--	--	1.33	1.33

*Computed

In Allende and Ambapur Nagla, a low density fraction has a very high Li enrichment. In Forest Vale no such enrichment was observed, probably masked by presence of lot of normal material (Plagioclase?). (The light fraction of Forest Vale amounted to 3 percent by wt. as compared to 0.18 percent for Allende and 0.24 percent for Ambapur Nagla). The same fraction is enriched in nitrogen for all the three cases. This type of lighter fraction is probably a common occurrence in all the meteorites, though we can not generalise on the basis of our limited study. A look at Table 4.11 reveals that graphite (or a carbonaceous phase) could be present in the lighter fraction. If it was really graphite, it would be extremely interesting in view of the 'graphite grain' hypothesis of Ramadurai and Wickramasinghe, 1975 and Dwek, 1978 to account for excess Li, Be, B in meteorites compared to the sun. A simultaneous enrichment of N and Li, two geochemically dissimilar elements is very hard to account for, on chemical grounds. The Li results on grain size fractions of Forest Vale and Ambapur Nagla are also suggestive of an exotic origin for the enrichments.

The $\rho < 2.55$ fraction of Allende in the HCl residue is most probably a hydrated siliceous stuff formed during the dissolution process, as a gelatinous suspension was noticed after 2 days of HCl treatment. The two fractions $\rho < 2.97$ (Plagioclase) and $\rho > 2.97$ (pyroxene) of the HCl residue for

all the three chondrites show that Li in plagioclase $>$ Li in pyroxene. With this and our Li result on hand picked Olivine from Ambapur Nagla, it can be probably generalised that for chondrites $(Li)_{olv.} > (Li)_{plag.} > (Li)_{pyrox.}$

In Shalka diogenite the whole sample was in $\rho > 2.97$ fraction, even after HCl dissolution. Both fractions have the same Li. In eucrites the bulk samples have Li enrichment in the density fraction corresponding to plagioclase. But the enrichment vanished after HCl treatment. This shows that Li is associated with a HCl soluble phase which has a density between 2.55 - 2.97. Shukla and Goel, 1980 (preprint) noted a correlation between Ca and Li and Al and Li, and an anti-correlation between Mg and Li, in achondrites and suggested plagioclase as the carrier phase of Li. It is a well known fact that Li, because of its incompatible character gets strongly enriched in the residual liquids, similar to REE, during the differentiation processes. Li enrichment in KREEP rich lunar samples (Eugster, 1971) is an evidence for this fact. Though Ba and Eu are known to be concentrated in plagio-clase in the eucrite Juvinas (Schnetzler and Philpotts, 1969) because of their +2 oxidation state, the rest of the REE with their +3 oxidation state are concentrated in the pyroxene in Juvinas. Our results indicate that Li is not enriched in pyroxene of eucrites. Hence, Li might be carried by a minor phase which is HCl soluble and has a density between 2.55 - 2.97 g/cc. This observation together with (Shukla and

Goel, 1980) the observed correlations can be taken to indicate that this minor Li bearing phase is associated with Plagioclase in eucrites.

In the Abee sample the lighter fraction ($\rho < 2.97$) has slightly higher Li compared to the heavier one. Li is concentrated in the sulphide phase in E-chondrites (Nichiporuk and Moore, 1970). This sulphide phase is probably Oldhamite (CaS) having a density of 2.58 g/cc and thus can go with $\rho < 2.97$ fraction. On HCl dissolution both density fractions have the same Li, which is higher than the bulk Li value. Obviously a Li poor phase got dissolved in HCl treatment. Most probably this Li poor phase is the metal phase which is exclusively Kamacite for Abee (Rambaldi and Cendales, 1980).

4.2.5 <u>Lithium in magnetic and non-magnetic fractions</u> : In all the meteorites studied, irrespective of the class to which it belongs, Li is more in the non-magnetic portion compared to the magnetic portion, for the bulk meteorite. This is consistent with the lithophile character of Li in chondrites and achondrites and the chalcophile character in E-chondrites (Abee). The ratio Li_{nm}/Li_m ranges from nearly one for Allende, Ambapur Nagla and Paragould to as high as 5 for Allegan. In view of the fact that ^3H escapes from the metal phase in iron as well as stone meteorites (Fischer, 1967) the ^3H produced in $^6Li\ (n,\alpha)^3H$ might have escaped from the metal part of the magnetic portion thereby giving an apparently lower Li in the

magnetic portion and a higher value for the ratio Li_{nm}/Li_m.
This seems to be the case for Allegan. In cases where the
ratio is not very high (Ambapur Nagla etc.) it may be that
either the metal content of the magnetic portion is not
appreciable or the metallic grains are embedded in a matrix
where ^3H can be effectively retained.

4.2.6 <u>Lithium in sieve fractions</u> : The meteorites analysed
for N have all been studied for Li. The sieving studies
might indicate the presence of irradiated'interstellar gra-
phite grains' in the meteorites as proposed by Dwek, 1978.
The carbonaceous chondrites with their primitive character
would be the natural choice for such a hunt. The most pro-
bable size for such grains will be a radius of $\sim$ 1 μm
(Campbell et al., 1976). The Li data on sieve fractions are
presented in Table 4.10. The various meteorite groups will
be discussed separately.

<u>Carbonaceous Chondrites</u> : The Li results are plotted against
m.g.d. in Fig. 4.9. Orgueil and Cold Bokkeveld have a flat
distribution. Even in Murray, Murchison and Allende magnetic
and non-magnetic fractions, though there is an occassional
slight enrichment, there is no definite trend. And most
important of all, the fine grain fraction has no enrichment
of Li as expected.
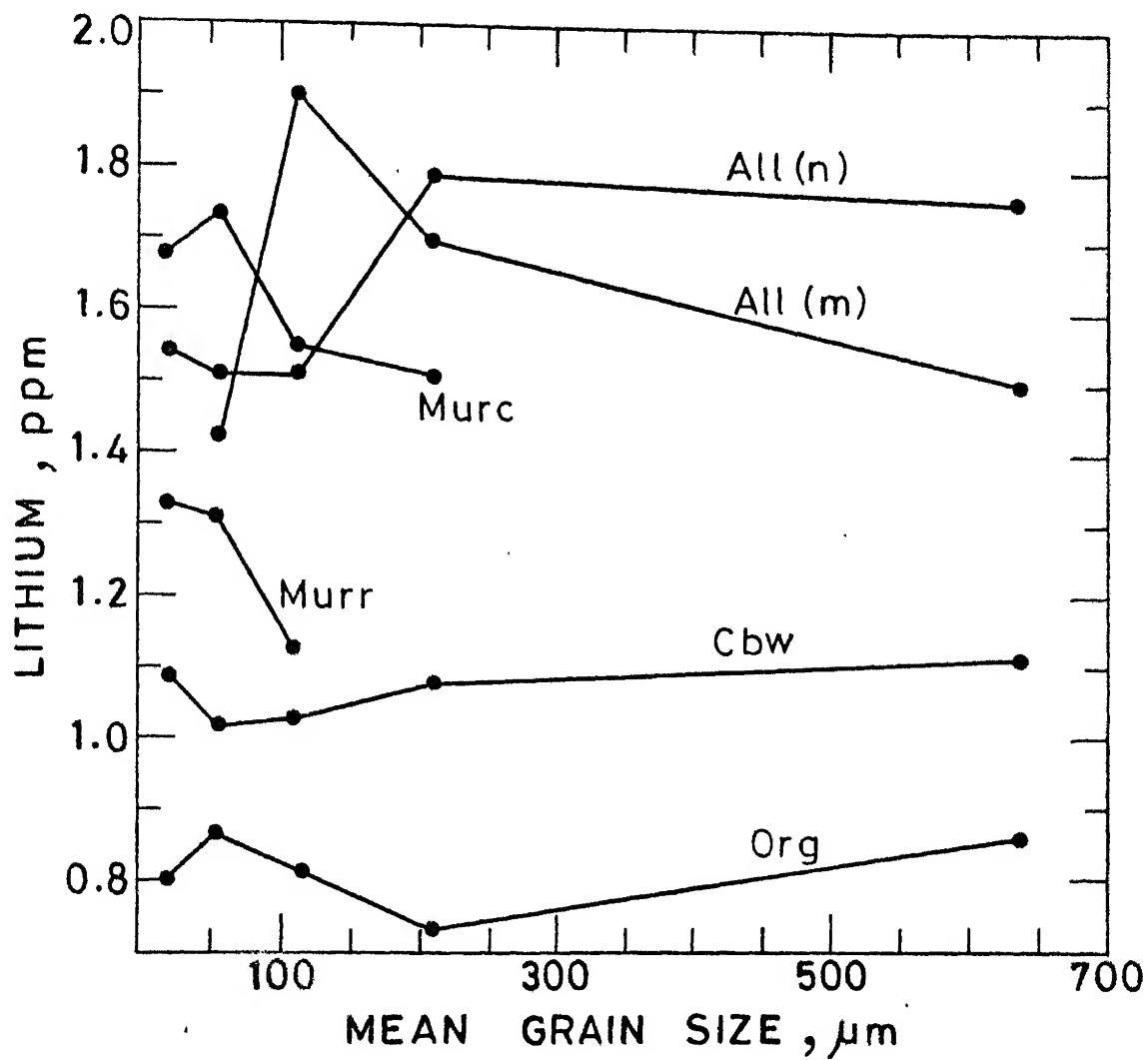
Fig.4.9   Li vs. mean grain diameter for
carbonaceous chondrites.

<u>Gas-rich meteorites</u> : The Li data for gas rich meteorites are shown in Fig. 4.10 as Li vs.m.g.d. plot. The magnetic portions show irregular trends. The fine fractions of Fayetteville and Pultusk have lower Li while the rest of the fractions show a gradual decrease of Li with increasing grain size. In St. Mesmin magnetic portion, Li increases with increasing grain size. These features might be partly due to ^{3}H diffusion from metal and partly due to mineralogical effects. In all these three meteorites the non-magnetic fractions have more Li in the finest fraction as compared to the coarsest fraction. But the variation is irregular for Pultusk, while there is a gradual decrease with increasing grain size for St. Mesmin and Fayetteville. These trends could as well be a mineralogical consequence. But this enrichment could be due to the presence of a phase enriched in Li. A phase similar to Allende low density fraction might explain the simultaneous enrichment of N and Li.

<u>Carbon-rich meteorites</u> : Paragould and Allegan do not show any grain size dependence for Li both in magnetic and non-magnetic portions. Forest Vale non-magnetic portion shows an increase of Li with decreasing grain size (Fig. 4.12). The other meteorite known to have carbon enrichment Bjurbole also shows a trend similar to Forest Vale for Li. A comparison of the carbon enrichments reveals that though all these meteorites have carbon enrichments, in the finer fractions, only Bjurbole and Forest Vale have a steep variation with
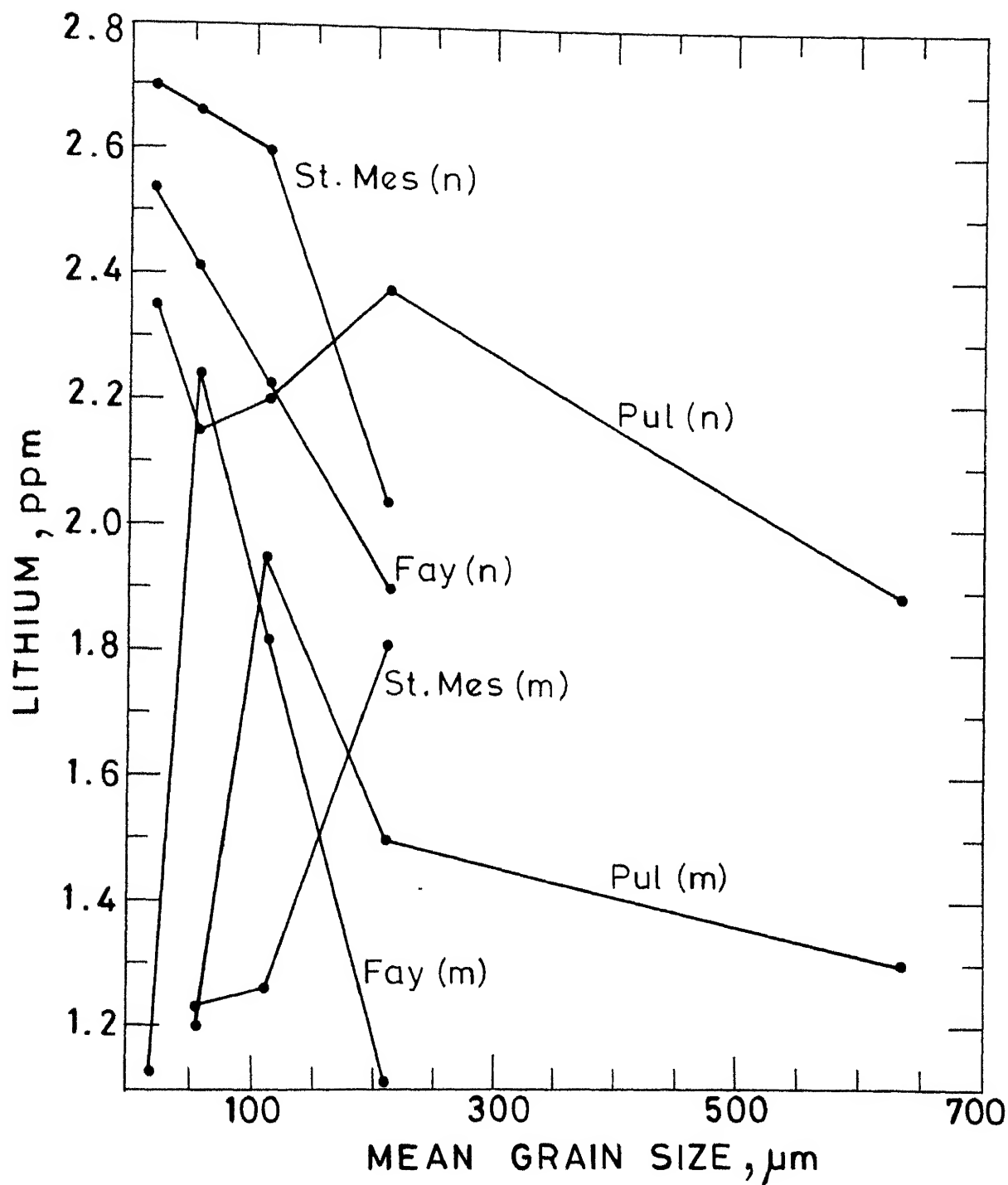
Fig.4.10   Li vs. mean grain diameter for
gas-rich meteorites.

grain size. This may be the reason why the Li enrichments are more revealing in these two cases. Also the shock history of Paragould could have disturbed th. features of the original Li.

Carbon was plotted against Li as shown in Fig. 4.8. A very good correlation can be noticed for both Bjurbole and Forest Vale. A correlation between Li vs. C in bulk meteorites did not exist (it has been tried). Quijano-Rico and Wänke, 1969 found a correlation of B vs. C and B/Li vs. C for chondrites which indicates the volatile nature of Boran and the constancy of Li in these meteorites. This is the first report of a correlated variation of Li and C in the same meteorite. Fredriksson and Nelson, 1969 have interpretted the carbon results as due to the presence of a carbonaceous matrix. This explanation cannot account for the Li enrichments observed. From the slopes of the straight lines in Fig. 4.8, values of 187.5 ppm Li/g. C and 1175 ppm Li/g.C are obtained for Forest Vale and Bjurbole respectively. Such very high Li contents cannot be explained on mineralogical grounds as C and Li have no common geochemical feature. The slopes of C vs. N plots (Fig. 4.7) give 2540 ppm N/g.C. for Forest Vale and 11,390 ppm N/g.C. for Bjurbole. The N/C and Li/C values for Orgueil are 26,935 ppm N/g.C. and 25.5 ppm Li/g.C. respectively. Hence, admixture of C1 type material can not produce the observed N and Li enrichments. Recently Ganapathy

and Larimer, 1980 have found an unusually carbon rich ($\sim$90%) material which was highly enriched in volatile elements compared to C1 values. This material probably is a late condensate. Late condensates have been suggested to account for the high volatile contents of Supshee and Krymka (Laul et al., 1973). The matrices of U.O.C. of type 3 suggest the presence of late condensate in them (Huss et al., 1981). It is probable that such late condensates rich in volatiles might be present in Forest Vale and Bjurbole. Enrichments of Zn and Pb (Fredriksson, 1973) along with C and N can be accounted in the fine fractions of these meteorites, by the admixture of a minor amount of the Abee type late condensate. But the Li enrichment remains unexplained by this. The C vs. Li correlation indicates that both Li and C enrichments have the same origin. It might be possible that Li enrichment is a mineralogical consequence and the C vs. Li correlation is fortutious. But such correlation for two meteorites might be too much of a coincidence. Probably Li also gets enriched in the late condensates! The late condensing phase enriched in C and N, may get enriched in Li if to this is added a small amount of primary condensate or presolar dust or the lighter density phase present in Ambapur Nagla and Allende.

<u>Other meteorites</u> : Fig. 4.11 shows the Li vs. m.g.d. plots for Saratov and Dhajala. Both the meteorites show irregular trends for magnetic as well as non-magnetic portions, probably due to
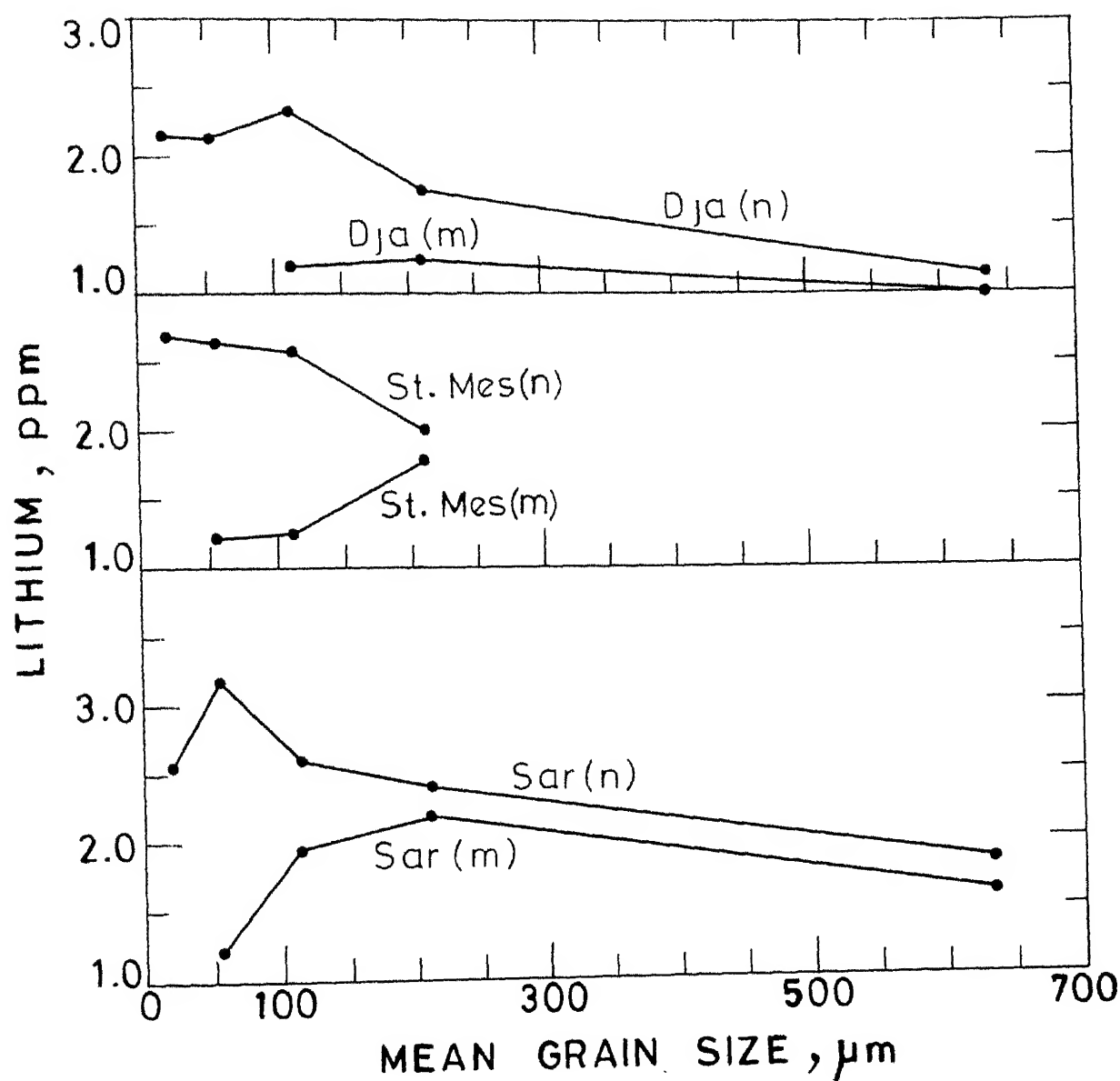
Fig. 4.11 Li vs. mean grain diameter for
ordinary chandrites .

mineralogical differences. The Shalka achondrite has only non-magnetic portion. The Li shows an increase with increasing grain size, though very slightly (Table 4.10).

The Ambapur Nagla meteorite is unique in a number of respects. Both the magnetic and non-magnetic portions show a grain size dependence for N, the magnetic portion showing unusually high enrichment of N. But only the magnetic portion shows an unusual high Li enrichment in fine grain fraction and Li vs. 1/r plot (Fig. 4.12) defines a straight line similar to Forest Vale. The non-magnetic portion shows almost same Li content in all size fractions. A repeat measurement to confirm the result gave the same trend (Table 4.4 and Table 4.10). Such high values of Li (164 ppm in one set and 41 ppm Li in the other set)in the finest magnetic fraction are unprecedented in meteorites. These Li values were obtained assuming a terrestrial value for $^7Li/^6Li$. It could be possible that, this unusual Li has a different $^7Li/^6Li$ ratio, so that the Li content falls in the normal meteoritic range,i.e.a ^6Li enrichment. It will be interesting to study Li isotopic ratio in this finest fraction. Another interesting fact is that out of 3 measurements on the finest magnetic fraction separated from three randomly picked pieces of Ambapur Nagla, always high N was found, but the Li content though high was highly variable (164.2 - 5.85 ppm). Most probably the Li enrichment is due to presence of Li rich grains which are smaller compared
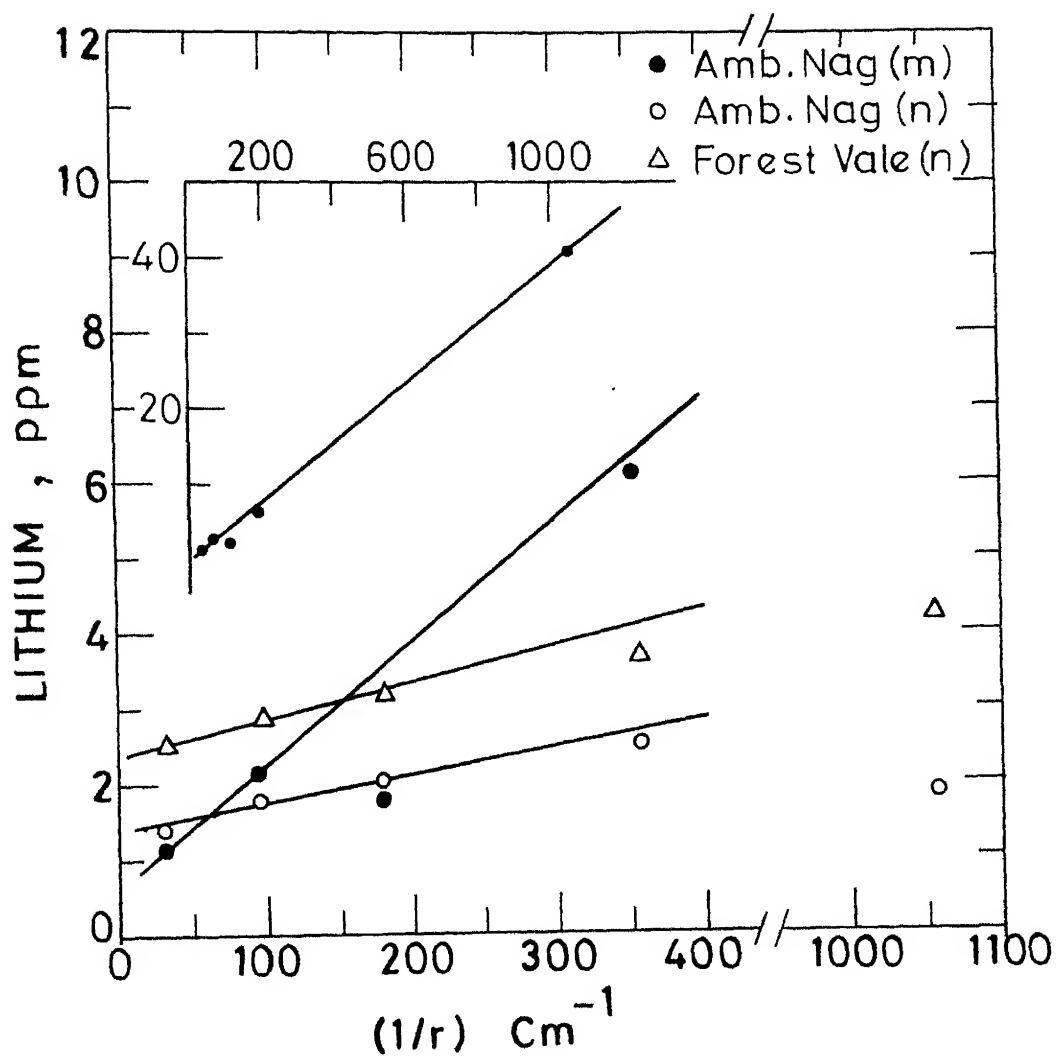
Fig. 4.12 Li vs. $\frac{1}{r}$ for Forest Vale and Ambapur Nagla.

to the range of ^{3}H produced in the reaction ^{6}Li $(n,\alpha)^3$H. These grains could be either free and just sticking to bigger grains of the meteorite or they are embedded in bigger grains. In cases where they are free the ^{3}H from them can escape out giving an apparent lower Li, while in cases where they are embedded, ^{3}H can be retained and higher Li value can be obtained. This ^{3}H escape problem will be further discussed in Chapter 5.

To check the possibility that N could be surface correlated a portion of $<38\mu$ mag. was leached with 1.5% HNO_3 for 2.0 hrs, wherein 50% of the sample dissolved. The residue was analysed for N. The results are shown in Table 2.3 (Chapter 2). Most of the N ($\sim$ 90 %) stayed in the residue. This shows that N is not implanted. Either a N mineral was present or N is occluded in the grains so that it was resistant to acid attack, similar to anomalous noble gases in the acid resistant carbonaceous phase in meteorites (Lewis et al., 1975). Also the late heating event as shown by loss of rare gases (Pellas et al., 1979; Zähringer, 1968) and the subsequent rapid cooling through 500°C (Hutchison et al., 1980) could not disturb the N in this phase. It is possible then that N is occluded in the grains. In view of the fact that such occlusions are possible in'interstellar grain clumps' (Abadi et al., 1976) it will be very interesting to further explore this possibility. Isotopic measurements of Li,

N and noble gases on this fraction will be very useful to characterize their origin.

4.3 Suggestions for Further Work

Li and N isotopic measurements on the finest grain size fractions would be highly interesting in characterizing the enrichments. A simultaneous C,Li and possibly B and Be measurement would be very fruitful. Noble gas measurements on the fine fractions and the light density fractions will surely reveal, if these fractions have any anomalous origin.

CHAPTER 5

STUDIES ON IRON METEORITES

Earlier studies of nitrogen in iron meteorites
(Gibson, 1969; Gibson and Moore, 1971b; Kothari and Goel,1974;
Shukla, 1977; Shukla and Goel, 1981) have indicated large
dispersion within a meteorite. Similar dispersion has been
observed for Li (Shukla, 1977).Li in iron meteorites was
thought to be of spallogenic origin (Hintenberger et al., 1965;
Levsky et al., 1972; Brick and Allegre, 1980) and as such it
should be < 1 ppb. The Li data reported by Shukla, 1977 were
typically a few ppb. In Shukla's measurements there was a
possibility of contamination from the ^{3}H produced from the
stone meteorites and even the quartz vial when they are
irradiated together, since stone meteorites and quartz have
Li contents of $\sim 10^3$ higher as compared to iron meteorites.
We have repeated the Li measurements taking care of the conta-
mination problems, and found Li to be of the same range as
reported by Shukla, 1977 with large dispersion.

To understand the dispersion of N and Li we have studied
both these elements in separated phases obtained by acid
dissolution of the meteorite piece. The non-magnetic residues
where N,Li are highly enriched have been further studied for
Xe (by Shukolyukov and Minh) and Os isotopes. First the N and
Li results in bulk iron meteorites will be presented and then

the results on separated phases will be discussed. The
classification, source and the types of inclusions present,
for the meteorites studied, are presented in Table 5.1.

5.1 Nitrogen in Iron Meteorites

N data on bulk meteorites are given in Table 5.2 and
Table 5.3. A good agreement between N data on irons from our
lab and those of Gibson and Moore, 1971b has been shown
(Shukla and Goel, 1981). Some pieces were etched with dilute
H_2SO_4 prior to analysis to remove $\sim$10% of the mass. Both
etched and unetched samples have similar N contents; demonstra-
ting the absence of surface contamination. Replicate measure-
ments indicate that all the meteorites studied show dispersion
in N contents. A careful inspection reveals that the dispersion
is more pronounced in IA and IIIA members. The nitride
carlsbergite (CrN) is abundant in IIIA group irons and to a
far lesser extent it occurs in IA and IIA also (Scot, 1973).
Its heterogeneous distribution in IIIA might be a reason for
N dispersion in this group. But even in IIIA, CrN rarely forms
when Ni content exceeds 8% (Scot, 1973). The meteorite
Alandroal which has 8.7% Ni (Buchwald, 1975) has accordingly
low N content (2.1 ppm) compared to the other IIIA members with
lower Ni content. But Alandroal has N contents varying by a fa-
ctor of 3. It has been suggested that N is favoured in the
taenite phase of iron meteorites (Goldschmidt, 1967; Gibson, 1969).

Table 5.1   Details of the iron meteorites studied

Meteorite	Class	Fall/Find	Source and Cat.No.	Inclusions Present*
Bogou	IA	Fl	Dr. Arnold	T,H,Co,G,S
Canyon Diablo	IA	Fd	AML	T,H,Co,Cg,G,S
Campo del Cielo	IA	Fd	Prof. Kohman	T,H,Co,G,S
Mazapil	IA	Fl	BNL, 1885	T,G,C
Odessa	IA	Fd	AML	T,H,Co,G,Gc,S
Ogallala	IA	Fd	Dr. Moore, # 112a	T,Co,G,Gc,S
Toluca	IA	Fd	Dr. Olsen # Me 1220	T,H,Co,G,S
Coahuila	IIA	Fd	Dr. Pellas # 727M	T,H,Co,(S)[1]
Mt. Joy	IIB	Fd	Dr. Kurat,Vienna	T
Navajo	IIB	Fd	Dr. Olsen # Me 2099C	Co
Sikhote Alin	IIB	Fl	Dr. Krinov, 2052	T,Co,S
Carbo	IID	Fd	Dr. Moore 494.1X	T,H
Tobychon	IIE		USSR	T
Alandroal	IIIA	Fl	Dr. C. Teixeira Portugal	T
Cape York	IIIA	Fd	Dr. Buchwald	T,Cr
Davis Mountains	IIIA	Fd	Dr. Olsen # Me 2107	T
Henbury	IIIA	Fd		T,Cr
Kenton County	IIIA	Fd	Dr. Olsen # Me 135	T,(Co),Cr
Gibeon	IVA	Fd	Dr. Arnold	T,S
Chinga	IVB-An	Fd	Dr. Krinov # 529	T
Santa Cathorina	Anom.	Fd	Dr. Pellas, # 1289	T,S

[1]. Parentheses indicate occasional occurrence.   T = Troilite, C = Carbides, Co = Cohenite, Cg = Carbide under decomposition to graphite, Cr = Carlsbergite, H = Hexonite, G = Graphite, Gc = Graphite with distinct Cliftonite development, S = Silicates

*From Buchwald, 1975, Vol. 1.

Table 5.2 Nitrogen and Lithium in iron meteorites

Meteorite	N(ppm) Replicate	N(ppm) Mean	^{6}Li(ppb) Replicate	^{6}Li(ppb) Mean
Bogou	324.0,345.5 2.6, 33.3 61.6, 39.7 55.5, 71.1 24.2, 35.8	99.3	1.4 0.8,0.5 0.5,0.4 0.5, 0.6 0.5, 0.4	0.6
Ogallala, '' etched	51.2, 19.5 50.0*	40.2	2.2, 1.9 2.2*	2.1
Coahuila	6.3, 4.0 3.0, 2.3* 2.3*	3.6	0.3, 0.5 0.3, 0.02* 0.1*	0.2
Navajo	33.3, 9.4 6.7,12.0 5.9, 9.0	12.7	1.5, 0.9 1.4, 1.0 0.3, 0.06	0.8
Mt.Joy,	--	--	0.9	0.9
Carbo	38.3,34.1 6.0	26.1	1.3, 1.4 1.0	1.2
Kenton County	42.0,33.0	37.5	0.2, 0.2	0.2
Chinga	14.5,33.4* 4.7*,4.2*	14.2	0.7, 0.1* 0.08*,0.13*	0.25
Santa Catho-rina	12.0, 9.9 10.8, 7.2 7.8*,10.0*	9.6	0.6, 0.7 1.2, 1.0 0.5*,0.04*	0.7
d'Alandrol	3.5, 1.9 1.8, 1.1	2.1	0.13,0.07 0.04,0.03	0.06

*etched with dil.H_2SO_4 to remove surface material.

Table 5.3   N,Li in iron meteorites irradiated in
            aluminium capsule

Meteorite	N(ppm)	^{6}Li(ppb)
Bogou	88.9, 55.0	0.16, 2.5
Campo del Cielo	23.7, 50.9	0.7 , 2.8
Canyon Diablo	25.8, 41.7	3.4, 0.7
Odessa	92.5, 57.9 74.3	5.4, 3.4 1.4
Toluca	96.3	2.3
Coahuila	5.3, 6.6	0.11, 0.11
Navajo	10.8, 9.8	0.4, 0.3
Tobycnon	7.2	0.9
Cape York	51.2, 38.1 36.2	0.14, 0.34 0.14
Davis Mountains	22.7	2.3
Henbury	10.5	0.2
Gibeon	-- 2.7	1.4, 0.22
d'Alandrol	7.8	0.9
Santa Cathorina	21.9, 51.6	0.8, 0.8

Shukla and Goel, 1981 have suggested that the presence of taenite might be the reason for high N contents of IA irons. This is only a conjucture, from the fact that the volatile Ga is enriched in taenite (Rambaldi and Cendales, 1979; Reed and Enright, 1981), but no N data exist for taenite of iron meteorites. Also presence of taenite in IA does not explain the dispersion of N. We have analysed N in separated phases of iron meteorites to understand the cause for its dispersion. N in separated phases will be discussed in a later section.

5.2 Lithium in Iron Meteorites

We report our Li data as ^{6}Li, in view of the unknown isotopic ratio for Li in iron meteorites. If a normal (terrestrial) isotopic ratio is assumed, 12.5 x ^{6}Li gives the total Li. Our results are given in Table 5.2 and Table 5.3. There was no Li work in iron meteorites, in the literature, except that of Fireman and Schwarzer, 1957. These authors have only indicated that the ^{6}Li contents in four iron meteorites were < 1 ppb. Krankowsky and Müller, 1967, measured Li in the troilite nodules of Odessa and reported a value of 40 ppb. Our data also show that ^{6}Li in irons is around 1 ppb. But similar to N, ^{6}Li also varies between different groups, among the member of the same group and also within a meteorite.

In our earlier measurements we were irradiating iron

meteorites, together with the stone meteorites and standards in a vacuum sealed quartz vial. In this environment all the other materials have a hundred fold excess of ^{6}Li compared to irons. Hence, a possibility of ^{3}H diffusion into iron pieces existed. This contamination possibly could give the irregular abundance pattern observed, although similar ^{6}Li contents of the etched and unetched pieces speaks against it. To be very sure about our data we have measured ^{6}Li in a fresh batch of samples, irradiated in a screw capped Al-capsule, avoiding the contact with Li rich materials. These pieces, after irradiation were etched with dil.H_2SO_4 to loose $\sim$10% mass, so that surface contamination if any is removed. ^{6}Li data on these pieces are given in Table 5.3. The data of these samples agree with the earlier measurements, indicating the absence of contamination. This set of ^{6}Li data is free from contamination problems. There is a good agreement between this set of data and the earlier set, demonstrating that our earlier ^{6}Li data are also free of contamination. But these ^{6}Li contents appear high, if Li is assumed to be of spallogenic origin in iron meteorites. Also the ^{6}Li/K ratios for iron meteorites are higher compared to other solar system materials (Shukla, 1977).

As earlier discussed (Chapter 1) there are two problems which come in the way of ^{6}Li determination in iron meteorites. They are : a) Interference from ^{3}He and b) Escape of ^{3}H from the iron matrix. Very fortunately the ^{3}H escape nullifies the effect caused by ^{3}He.

5.2.1 ^{3}He interference : Assuming that the neutron flux, to which we irradiate our samples, is mostly thermal, the production of ^{3}H from ^{3}He (or the apparent excess ^{6}Li) is given by

$$^6Li(excess)_{atoms} = {}^3He_{atoms} \times \frac{\sigma(^3He)}{\sigma(^6Li)}$$

which on simplification yields

$$^6Li(excess) = 0.015 \text{ X ppb}$$

where X = ^{3}He in 10^{-8} CCSTP/g.

In Fig. 5.1 apparent ^{6}Li [^{6}Li(original) + ^{6}Li(excess)] is plotted vs. ^{3}He. Curves are drawn for typical ^{6}Li(original) values of 0.1,1.0,10, and 100 ppb. The ^{3}He range covered in this figure is typical of iron meteorites. It can be seen that when inherent ^{6}Li is high or ^{3}He is low, interference is insignificant. On the other hand, when ^{6}Li is low and ^{3}He is appreciable, the ^{3}H is mainly due to ^{3}He. On the same plot the ^{6}Li contents of some iron meteorites are also plotted against their respective ^{3}He contents. It can be noticed that for large meteorites where ^{3}He is low (Canyon Diablo) the ^{6}Li is much higher than expected from ^{3}He while in small meteorites (Bogou, Carbo and Carlton) the ^{6}Li is much less compared to ^{3}He and serious interference is possible. Also it can be noted from Fig. 5.1, that the ^{3}H activity observed in high ^{3}He meteorites is much less than expected even from ^{3}He alone. In Table 5.4 the ^{3}He and ^{6}Li of the meteorites studied are given. If ^{3}He is interfering,high
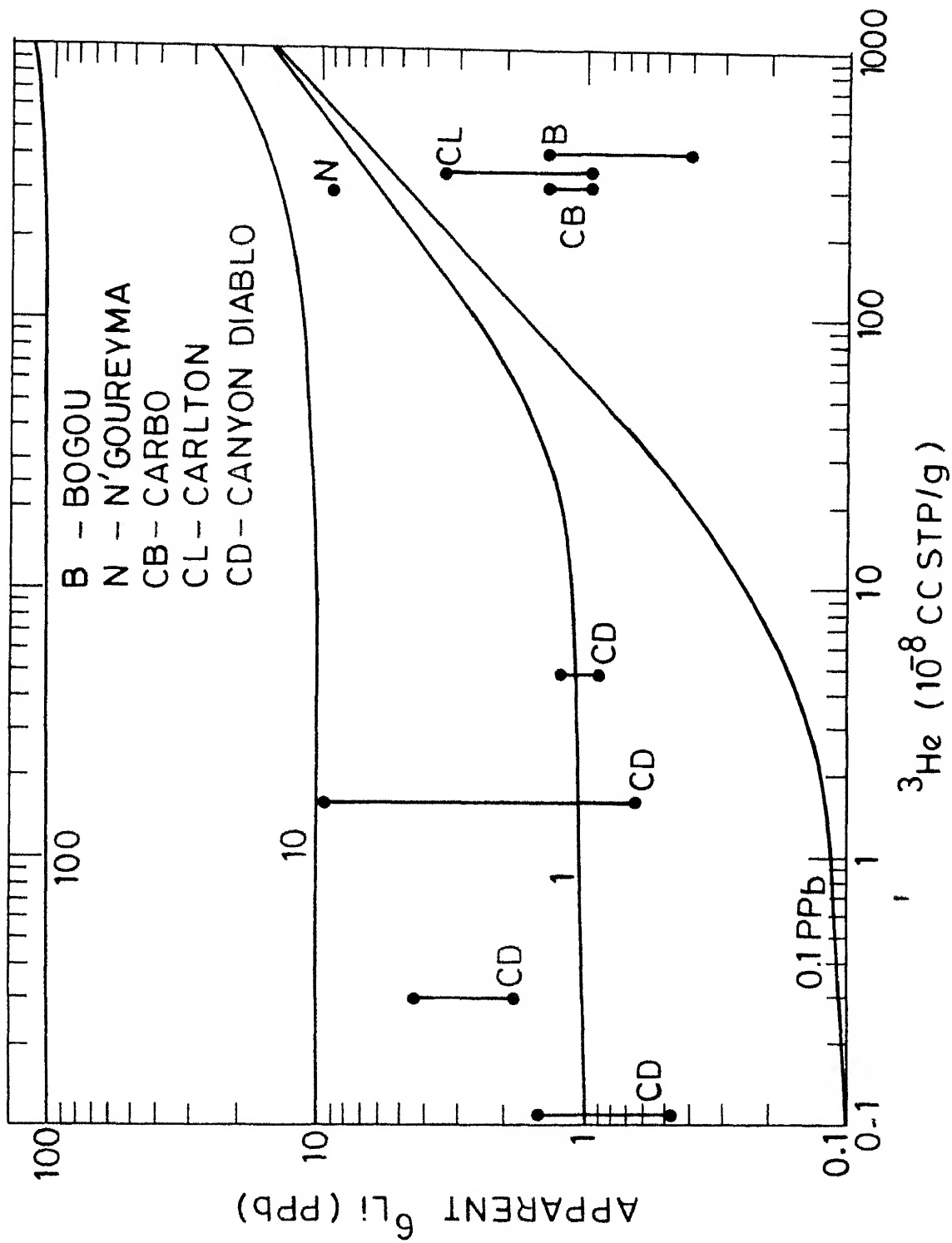
Fig. 5.1 ^{3}He vs. apparent ^{6}Li for iron meteorites

Table 5.4   Comparison of N,^{6}Li with Ir and ^{3}He

Meteorite	Ir(ppm)	^{3}He x 10^{-8} CCSTP/g	N(ppm)	^{6}Li(ppb)
Bogou	1.4	413	99.3	0.6
Canyon Diablo	1.9	--	33.6	2.1
Campo del Cielo	3.2	--	37.3	1.8
Odessa	2.2	1.6 -- 235	75.0	3.4
Toluca	1.8	1.42--100	96.3	2.3
Coahuila	15	--	3.6	0.2
Sikhote Alin	0.03	--	12.3	0.4
Carbo	13	315	26.1	1.2
Cape York	5.0	--	41.4	0.21
Kenton County	15	519	37.5	0.2
Gibeon	2.3	--	2.7	0.8
Chinga	3.6	219	14.2	0.25

Sources for Ir and ^{3}He data : Buchwald, 1975, Vol. 1 and Wasson,1974.

^{3}He should give high ^{6}Li. But no such relation is evident from Table 5.4. This might be due to the diffusion of ^{3}H from iron matrix (Fischer, 1967).

5.2.2 ^{3}H diffusion problem : It is well known that almost all the iron meteorites and the metal phases of ordinary meteorites, after their fall on earth, loose their cosmogenic ^{3}H by a slow diffusion process (Fischer, 1967). This process of diffusion is not significant, when the meteorite is in the interplanetary space, as evidenced from the expected ^{3}He/^{4}He ratios [since about half the ^{3}He in the meteorites comes from ^{3}H decay, the ^{3}He/^{4}He would have been effected very much in case of ^{3}H loss] (Signer and Nier, 1962).

Fischer, 1967 measured ^{3}H activity in irradiated Sikhote Alin over a period of several months and found that ^{3}H diffused out with a half time of $\sim$45 days. This was much faster than the cosmogenic ^{3}H diffusion in Sikhote Alin, which has a half time of $>$100 days. Also Dubost and Lefort, 1963 have found that in an irradiated iron-target ^{3}H diffusion has a half time of about 100 days. The above three curves (Figure 1 of Fischer, 1967) have been reproduced in Fig. 5.2. Wagener, 1967 estimated the time required for total release of ^{3}H after the fall (at room temperature) to be few months to years, depending upon the grain size of the meteorite. The above results indicate that 1) ^{3}H diffusion rate is dependant on the structure of the metal phase and 2) it is faster in irradiated matrix,

presumably due to the radiation damage, causing defects, which may be aiding diffusion process.

We have measured the ^{3}H activity of Bogou (fillings) at 3 different intervals of time after the irradiation. These results are plotted in Fig. 5.2. It is very clear that ^{3}H has diffused out and reached a plateau after $\leq$ 100 days. The diffusion trend in Bogou is similar to that of irradiated Sikhote Alin (curve 2), though the diffusion is faster in Bogou, presumably due to structural differences and the greater dose of irradiation in case of Bogou ($\curvearrowleft$ 10^{13} n cm^{-2}sec^{-1} for one month against 5×10^{11} n cm^{-2}sec^{-1} for 6 hrs in case of Sikhote Alin). Also our measurements on a number of iron meteorites at two different times separated by $\curvearrowleft$ 2 years gave the same ^{3}H activity (^{6}Li) (except for decay) as shown in Table 5.5. It is also evident from Table 5.5, that when the ^{3}He is less (C.D. samples) there is no change of ^{6}Li content with time, implying that a) the ^{3}He interference is insignificant and b) the ^{3}H originating from ^{6}Li does not escape, showing that it is trapped at a stable site (non-metallic grains). Also all diffusable ^{3}H (when ^{3}He is considerable) does so within a few months time, (our typical cooling period) and the ^{3}H activity that remains is due to ^{3}H trapped at stable sites.

But Fireman used the method ^{3}He (n,p) ^{3}H to map the ^{3}He distribution in Carbo (Fireman, 1958) and Grant (Fireman, 1959)
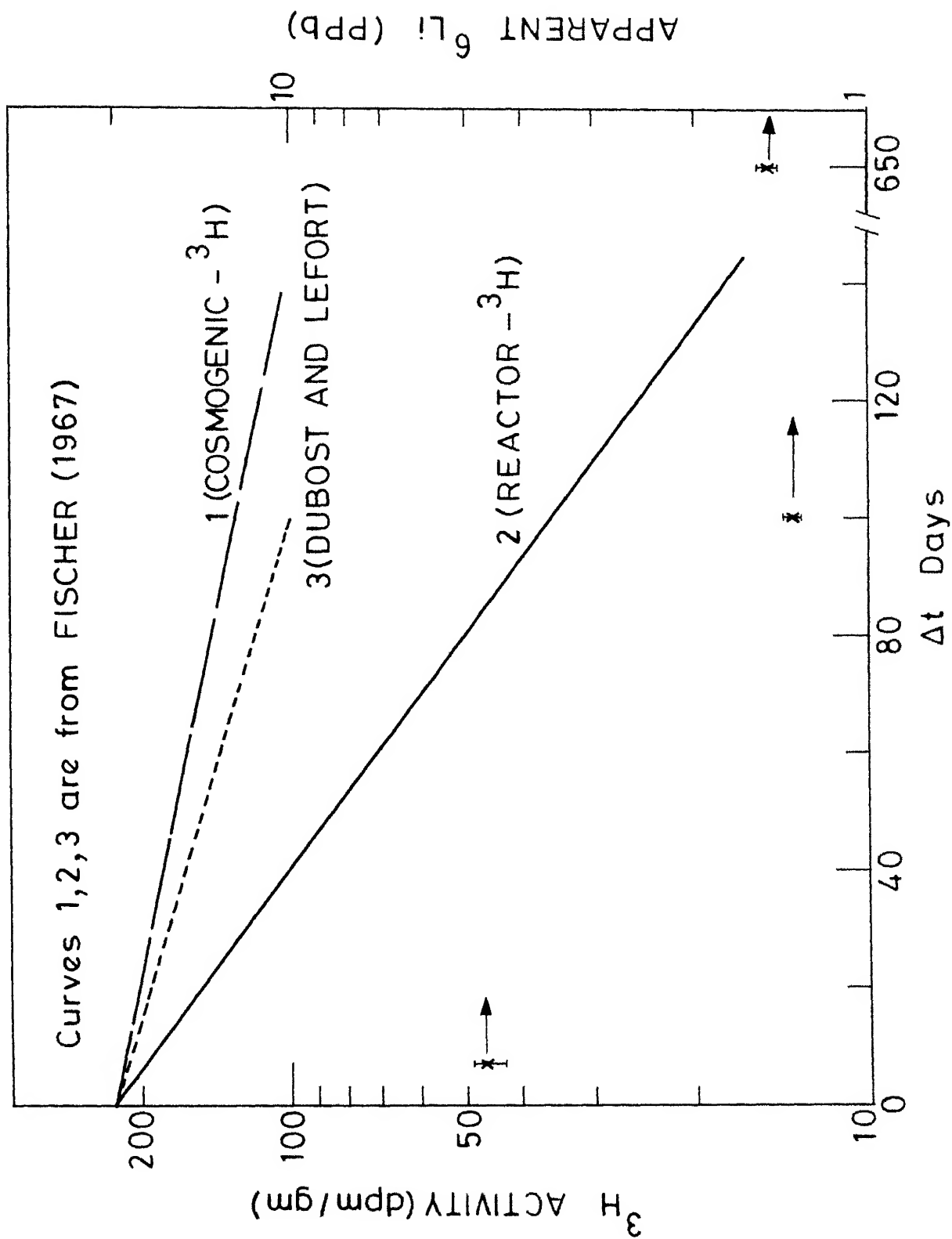
Fig. 5.2 ^{3}H activity as a function of time for Bogou.

Table 5.5 ^{6}Li (ppb) at different intervals of time after irradiation

| Meteorite | $\triangle t$(days) | | | ^{3}He x 10^{-8} CCSTP/g |
	7	650	2500	
Bogou (Fillings)	4.64	1.38 (100 days)	1.52 (1200 days)	413
Canyon Diablo unschocked	0.65,0.92	0.88~1.12	--	4.9
600 Kb	0.15	0.48~1.44	--	0.1
>1000 Kb	0.11,0.06	0.64 ~9.6	--	1.6
Mazapil	--	0.17 ~0.22	1.41	
Sikhote Alin	--	0.34 ~ 0.51	0.45	
Tobychon	--	0.18 ~ 0.66	0.52	
Henbury	--	0.03 ~ 0.06	0.30	

meteorites and obtained results consistent with other workers (Hoffman and Nier, 1958) indicating that ^{3}H diffusion had not affected his results. This might be due to presumably short time lag between irradiation and measurement of ^{3}H activity of various samples. The above arguments and our Bogou results clearly show that ^{3}H diffuses out of the metal phase of irradiated iron meteorites.

Coming back to the question of the effect of ^{3}H loss on the determination of ^{6}Li in iron meteorites, we recognize two extreme situations. If we suppose that all ^{6}Li is uniformly distributed in the metal phase, we must conclude that the ^{3}H produced from its irradiation would be mostly lost by diffusion This would be like ^{3}H loss that is generated from the activation of ^{3}He. Only a fraction that is trapped at grain boundaries might remain. The ^{3}H activity in such a case will have no relation to the amount of ^{3}He or ^{6}Li in the metal, but will be related to the presence of grain boundaries and trapping sites.

If Li is dispersed in iron meteorites in small non-metalli grains, the situation will be quite different. ^{3}H produced and retained in the grain will not be lost by diffusion. Moreover it would be essentially from ^{6}Li, since ^{3}He will be comparative too small in non-metallic grains. It would be possible in this case to measure the ^{6}Li in the meteorite. Fortunately, Li in ir meteorites is present in grains of non-metallic character (Section 5.5.3).

Therefore, even in small meteorites, having high ^{3}He, the ^{6}Li will have no serious interference, because the ^{3}H from ^{3}He diffuses out. Our ^{6}Li data represent the ^{6}Li embedded in grains. If the Li in the metal phase is not appreciable, then the ^{6}Li from grains alone will account for the total ^{6}Li of the meteorite. The dispersion of ^{6}Li might then be due to the heterogeneous distribution of the Li rich grains in iron meteorites.

5.3 Separation of Phases in Iron Meteorites

Phases are separated after irradiation. About 1 gm. irradiated piece is dissolved in excess of 4 M H_2SO_4. With occasional stirring, the dissolution is complete in 3 to 4 days. Completion of dissolution is gauged by clarity in solution without evolution of bubbles. The solution is decanted and the residue is washed with distilled water till free of acid and dried under heat lamp. With a hand magnet, the residue is separated into magnetic and non-magnetic portions. The non-magnetic residue (nmr) amounted to $\sim$ 1 mg/g and is always fine grained. The magnetic residue (mr) is considerable. In some cases, the mr has very big flakes. The flakes are separately analysed for N and Li. Table 5.6 gives the mass distribution of the various phases for the meteorites studied.

Two meteorites Canyon Diablo (CD) and Campo del Cielo (CdC) were dissolved prior to irradiation. The meteorite piece

Table 5.6 Mass distribution of various phases of iron meteorites

Meteorite	Starting Mass (mg)	Recovered Mass of		
		Flakes (mg)	Mag.Res. (mg)	Non-mag. res. (mg)
Odessa	1132.5	6.90	105.5	2.01
Toluca	847.5	12.35	1.26	0.32
Canyon Diablo	1809.0	20.60	113.0	2.70
Henbury	1863.0	12.44	3.56	1.84
Cape York	4861.0	81.15	3.30	3.04
Davis Mountains	1859.0	1.42	2.09	1.80
Sikhote Alin	936.0	16.50	0.30	0.17
Tobychon	762.0	19.62	--	--
Navajo	966.5	--	7.00	--

($\backsim$ 100 gm) is first cleaned of rust and any exterior material.
It is washed with petroleum ether, dried and thoroughly washed
with distilled water. This piece is etched with 2M H_2SO_4 to
remove first $\backsim$ 10 gm. or so of material and then washed with
distilled water and dried. This is finally dissolved in
4M H_2SO_4. With occasional stirring and frequent change of the
acid, the piece dissolves in about 10-15 days. The residue is
washed free of acid, dried under heat lamp, and separated into
magnetic and non-magnetic residues.

5.4 Physical Characteristics of the Residues

The residues obtained from CD and CdC, prior to irradiation,
have been investigated by X-ray diffraction and EPR spectroscopy.
The mr of CdC is mostly schreibersite as shown by its X-ray
spectrum. There are no flakes in CdC. The flakes of CD gave an
X-ray diffraction pattern which does not match with taenite or
any known magnetic mineral of iron meteorites. The nmr of both
meteorites are unidentifiable as they give only one peak in
case of CdC and a small bump for CD. The X-ray spectra of
non-magnetic portions from two bulk inclusions of CD also show
no peaks. In Table 5.7 the d values of the spectra obtained as
well as the d values of some meteoritic minerals are given.
Most probably, the nmr of C.D. is graphite, as 'graphite of
iron meteorites may be amorphous' (Mason, 1962). Also acid
resistant 'residues' of iron meteorites were shown to contain
carbon by Deines and Wickman, 1973.

Table 5.7   Results of X-ray diffraction studies of
            residues

Sample		d values (intensity)
Campo del Cielo	M	2.18(100); 2.10(70); 1.96(70); 2.12; 2.02; 1.83; 1.76
''	N	3.32 (100)
Canyon Diablo	F	2.06 (100); 1.03(25); 2.12(20)
''	M	2.11 (100)*
''	N	2.10 (100)*
'' Inclusion	N	2.09 (100)*
Meteoritic minerals[**]		
Kamacite		1.17 (100); 2.02(90); 1.43(70); 1.01(70)
Taenite		2.06 (100); 1.07(40); 1.78(30); 1.27(20)
Troilite		1.06 (100); 2.63(80); 1.04(80); 2.97(60) 1.72 (60)
Graphite		3.36 (100); 1.67(80); 2.03(50); 1.16(50) 1.23 (20)
Schreibersite		2.19 (100); 2.11(70); 1.97(70); 2.13; 2.02; 1.83; 1.76.

F = Flakes; M = Magnetic Residue; N = Non-magnetic Residue

[*]   These peaks are small bumps

[**] From Hurlbut and Klein, 1977.

The nmr of both CD and CdC show the presence of free radicals as found by EPR spectroscopy. The EPR spectra are given in Fig. 5.3. The nmr of CD has a g value of 2.0665 while that of CdC has a g value of 2.1357. The g value of DPPH is 2.0037. The g value of CD nmr is like that of DPPH, a π radical. This indicates that the free radicals are due to the presence of organic compounds in the nmr. It may be mentioned here that in a later dissolution process some oily organic compound was noticed to be floating in the solution. This has been extracted with benzene and its characterization is in progress. It might be that the non-magnetic residues have a minor component that has free radicals. Interesting enough, the non-magnetic portions of the bulk inclusions of CD show no signal in their EPR spectra. The non-magnetic portion of Ambapur Nagla shows a broad hump, typical of silicate structure. These spectra are also given in Fig. 5.3. These observations indicate that the nmr is different from the bulk inclusions. Deines and Wickman, 1973 also conclude the same on the basis of carbon isotopic data. These authors have attributed the carbon isotopic differences, to the presence of 'fossil' carbon which is isotopically heavier. This 'fossil' carbon might be the carrier of the free radicals and the other anomalous features also as will be discussed.

The γ-spectra for all these residues after irradiation are recorded. In Fig. 5.4 the γ-spectra for the nmr of 3IA irons
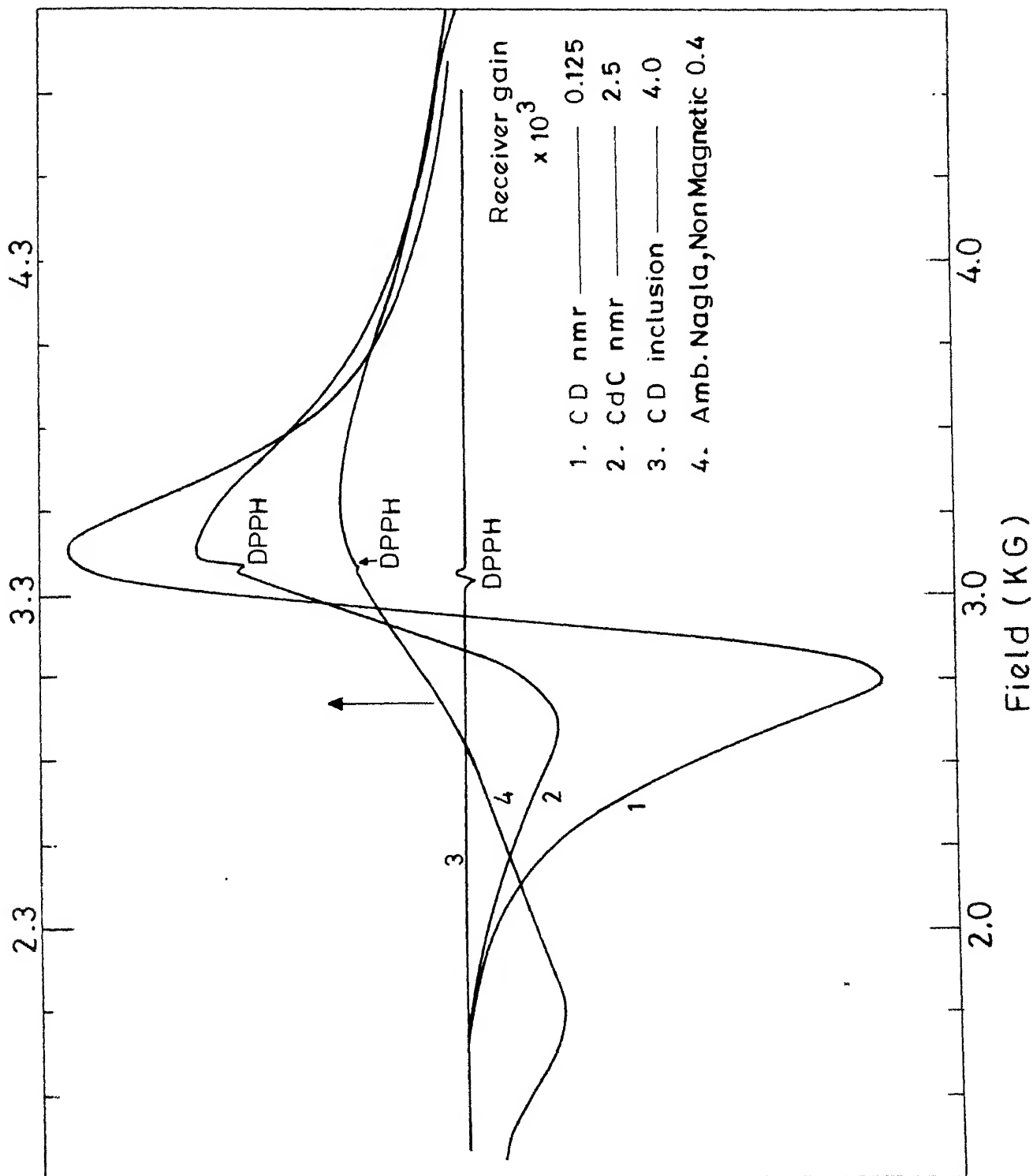
Fig. 5.3   EPR spectra of residues.
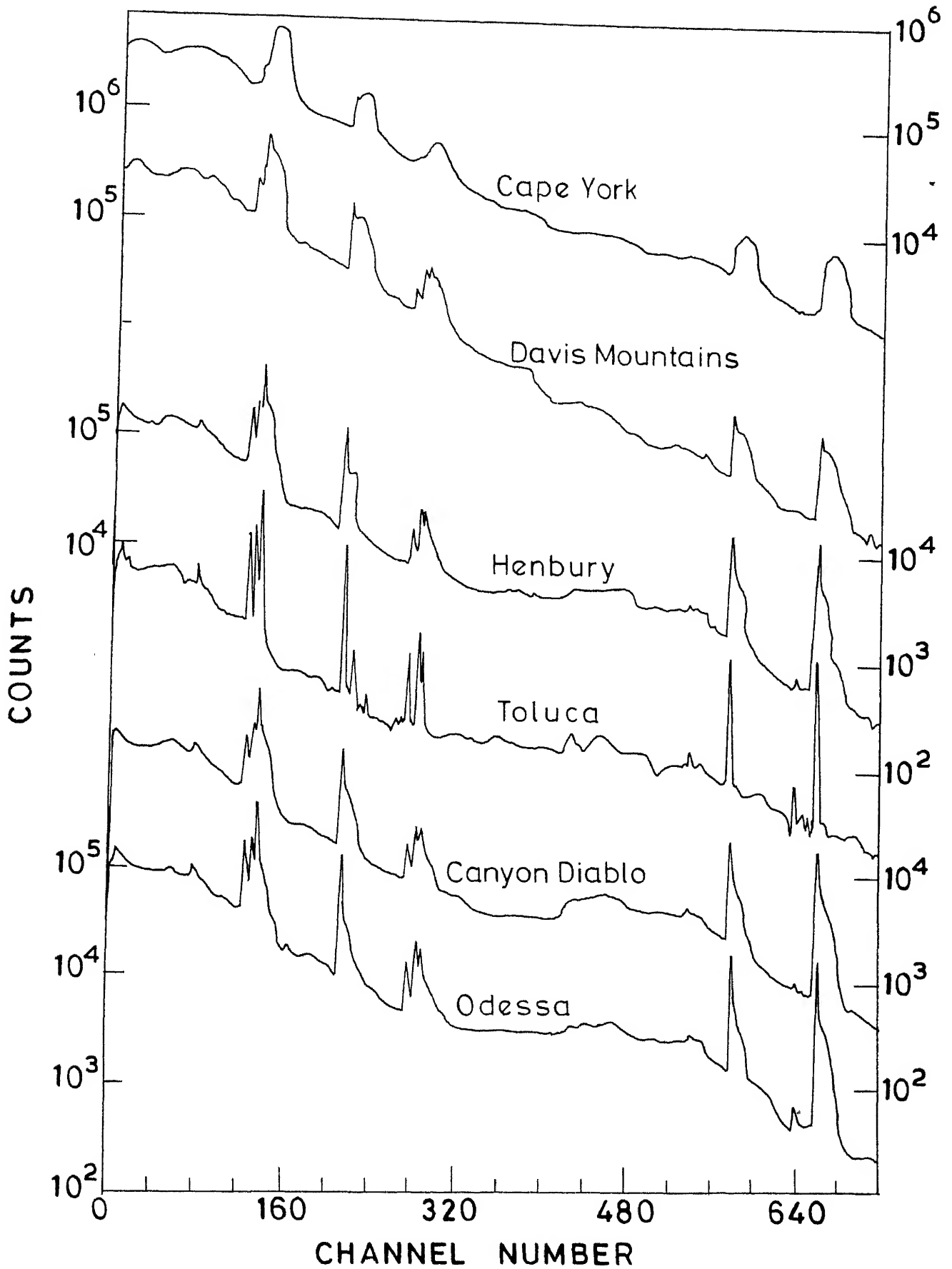
Fig.5.4   γ- Spectra of irradiated non-magnetic residues .

and 3 IIIA irons are given. A similarity can be noticed among the IA residues and among the IIIA residues.

5.5 Results of the Residues

5.5.1 Fe, Co and Ir : Data on the separated phases are given in Table 5.8. Because there is no Ir standard in this batch of irradiation (BCR-1 has a very low and uncertain Ir content) we reported our Ir data relative to flakes of each meteorite. Also given are Ir values with respect to Odessa magnetic residue, which will serve the purpose to look for trends with respect to Ir. As there is no similar data on N and Li, in the literature only Fe and Co can be compared. Jochum et al., 1980 have analysed trace elements in schreibersite of iron meteorites. We have identified our CdC, mr to be schreibersite. Hence our CdC values can be compared. Our Fe and Co values are, less by a factor of 2 (for Co) and factor of 4 (for Fe), compared to Jochum et al., 1980. It might be that during the dissolution process Fe and the associated Co are leached out by H_2SO_4.

In general the nmr has low Fe and high Ir compared to the other two phases. In some cases the Ir enrichment is by large factors (85 for CD and 100 for Henbury) relative to flakes. The Co contents are more in some cases and less in the rest. The two sets of results from CD, one set on phases separated prior to irradiation, and the other set on phases separated from irradiated piece are similar (except for [6]Li) indicating that there is no contamination during the dissolution stage in

Table:5-8 Data on seperated phases of iron meteorites
(B=Bulk ; F=Flakes ; M=Magnetic residue ; N=Non-magnetic residue)

Meteorite	Phase	N (ppm)	^{6}Li (ppb)	Fe (%)	Co (ppm)	Ir Relative	Ir Relative to *
Odessa	B	73.0	2.5		269.3	1.00	15.0
	F	320.4	38.2	15.00	491.3	0.06	1.0*
	M	38.0	7.6	26.88	500.9	17.61	258.0
	N	1450.0	66.3	4.00			
Toluca	B	96.3	2.3		378.0	1.00	4.7
	F	649.4	4.5	13.25	587.0	24.89	118.7
	M	791.2	17.8	7.60	200.0	13.77	65.7
	N	5496.8	90.4	7.70			
Canyon Diablo	B	34.7	1.9		217.8	1.00	2.3
	F	64.2	16.5	13.96	386.5	1.06	2.3
	M	52.8	8.4	21.66	439.5	85.50	193.0
	N	719.0	47.0	1.38			
Henbury	B	10.5	0.2		359.1	1.00	2.7
	F	144.2	10.9	10.53	217.0	43.55	108.7
	M	735.4	90.4	1.86	473.9	102.10	254.0
	N	1454.7	97.6	4.56			
Cape York	B	51.2	0.2		823.8	1.00	
	F	1190.5	1.9	21.35	156.0	2.94	
	M	422.1	11.4	1.98	---	1.87	
	N	292.8	31.4	3.38			
Davis Mountains	B	22.1	2.2		491.0	1.00	
	F	2596.2	9.8	20.07	40.8	0.41	
	M	3676.9	19.0	2.10	30.7	0.37	
	N	3715.5	31.4	1.84			
Sikhote Alin	B	12.3	0.4		439.0	---	
	F	56.4	39.6	---	478.5	---	
	M	193.0	93.4	---	1120.2	---	
	N	1193.4	70.7	---			
Tobychon	B	7.2	0.9		193.7	---	9.3
	F	44.6	5.0	6.68			
Navajo	B	10.0	0.3		364.1	---	7.0
	M	156.6	5.7	14.17			

When phases are seperated prior to irradiation

Meteorite	Phase	N (ppm)	^{6}Li (ppb)	Fe (%)	Co (ppm)	Ir Relative	Ir Relative to *
Canyon Diablo	B	34.7	1.9		502.4	1.00	
	F	59.2	26.5	26.30	689.0	0.41	
	M	37.8	20.2	34.40	230.7	3.45	
	N	609.6	860.0	1.51			
Campo del Cielo	B	37.3	1.8		514.0		Sc(ppm)
	M	264.8	280.0	14.22	168.0	1.00	1.1
	N<75µ	362.5	824.0	1.17	78.7	0.95	1.7
	75 – 270µ	305.7	754.0	0.95	18.0	0.32	3.7
	>270µ	338.0	1133.0	0.61		0.04	5.0

Error is < 1% for Fe,Co,Ir,and < 5% for Sc

either set, in set one from reagents, and in set two from hot
atom processes. Bild and Robinson, 1979 have found Metal/Silicate
partition coefficients of 70 for Mundrabilla Ir. They explained
such a low value for this partition for such a highly siderophi-
lic element, as due to the remains of early refractory condensa-
tes trapped in silicates condensing soon after. In our nmr the
situation is reverse. It is enriched in Ir compared to flakes
and mr. The nmr might have primordial refractory metal parti-
cles of the sort found in Allende inclusions (Blander et al.,
1980). High Os and Ir have also been found in HF, HCl resistant
carbon rich phases of Allende (Jovanovic and Reed, 1980), that
carry the anomalous noble gases. Our nmr also carry anomalous
Xe and possibly Os as will be discussed. Fe values of nmr are
also of the same order, as those of C-rich residues (Jovanovic
and Reed, 1980) and also of the metal rich alloy of Blander
et al., 1980.

The CdC nmr is different from the rest in appearance (it
looks grey and coarse while the others look black and fine
grained). The bulk silicate inclusions of CdC also are different
from the rest of IA silicate inclusions (Bild, 1977a; Robinson
and Bild, 1977; Wlotzka and Jarosewich, 1977) in that, they are
fractionated due to a slight igneous activity at a later stage,
as evidenced by the remelted plagioclase, and REE and other
trace element patterns. Also these inclusions were shown to
have surface correlated Xe and Kr (Hintenberger et al., 1969)

We have sieved our CdC nmr into three size fractions and analysed the elements in them. Except N and Li which do not show any grain size effect, the rest of the elements do show a surface correlation. Fe, Co and Ir decrease with increasing grain size while Sc shows the opposite effect. This might be due to the fine grained nature of the grains carrying metal rich particles which got sorted into the fine fraction. Sc is a lithophile element and its presence indicates silicate material. Most probably the nmr of CdC is an admixture of fine grained anomalous residue and small silicate inclusions which are coarse. This explains the increasing Sc content with grain size. The Xe and Kr results of Hintenberger et al.,1969 might then be due to the enrichment of these species in the same grains that carry the metal rich particles. Hintenberger et al., 1969 also have suggested that 'the grain size dependenc observed could perhaps be due to a high concentration of Kr and Xe in a mineral phase which is enriched in small.grain-size fractions'. This means that the anomalous fine grained materia could be present even in bulk inclusions. It is very much possible, but due to the dilution by normal silicate material, their effect can be seen for very sensitive elements like the noble gases. The ten fold excess of Xe in the nmr of CdC compared to the mr further strengthens the possibility that the grains are carriers of Xe and Kr.

5.5.2 <u>Nitrogen</u> : There are no flakes found in Navajo and CdC and all the magnetic residue is flakes in Tobychon. It can be seen that, compared to the bulk, N is more in the separated phases (except the mr of Odessa). In all meteorites, flakes have higher N. The flakes most probably are taenite lamellae. Their higher N content then is in accord with the expectation of Gibson, 1969 on the basis of solubulity. It could also be possible that the N rich grains are embedded in taenite. Small amount of carbon is known to be present in taenite, in solid solution (Deines and Wickman, 1973). The N enrichment in all magnetic residues (except that of Odessa) also might be, due to embediment of grains similar to nmr. The presence of N rich nmr in most of the irons studied gives an indication it might be a general phenomenon with most iron meteorites. The N enrichment in IIIA irons in which CrN occurs should be inter- preted with caution. But CrN is more prevalent in the kamacite (Buchwald, 1975) which dissolves during dil.H_2SO_4 attack. Still, it might be possible that some CrN is present in flakes and mr which give higher N contents. But a similar high [6]Li content of these phases points out that the enrichments are due to N and [6]Li rich grains. Further support to this view- point comes from the correlation of N vs Ir for the various phases (Fig. 5.5). Except Toluca nmr which has by far the highest N, all the other points in Fig. 5.5 define a positive correlation. Such a correlation does not exist for bulk
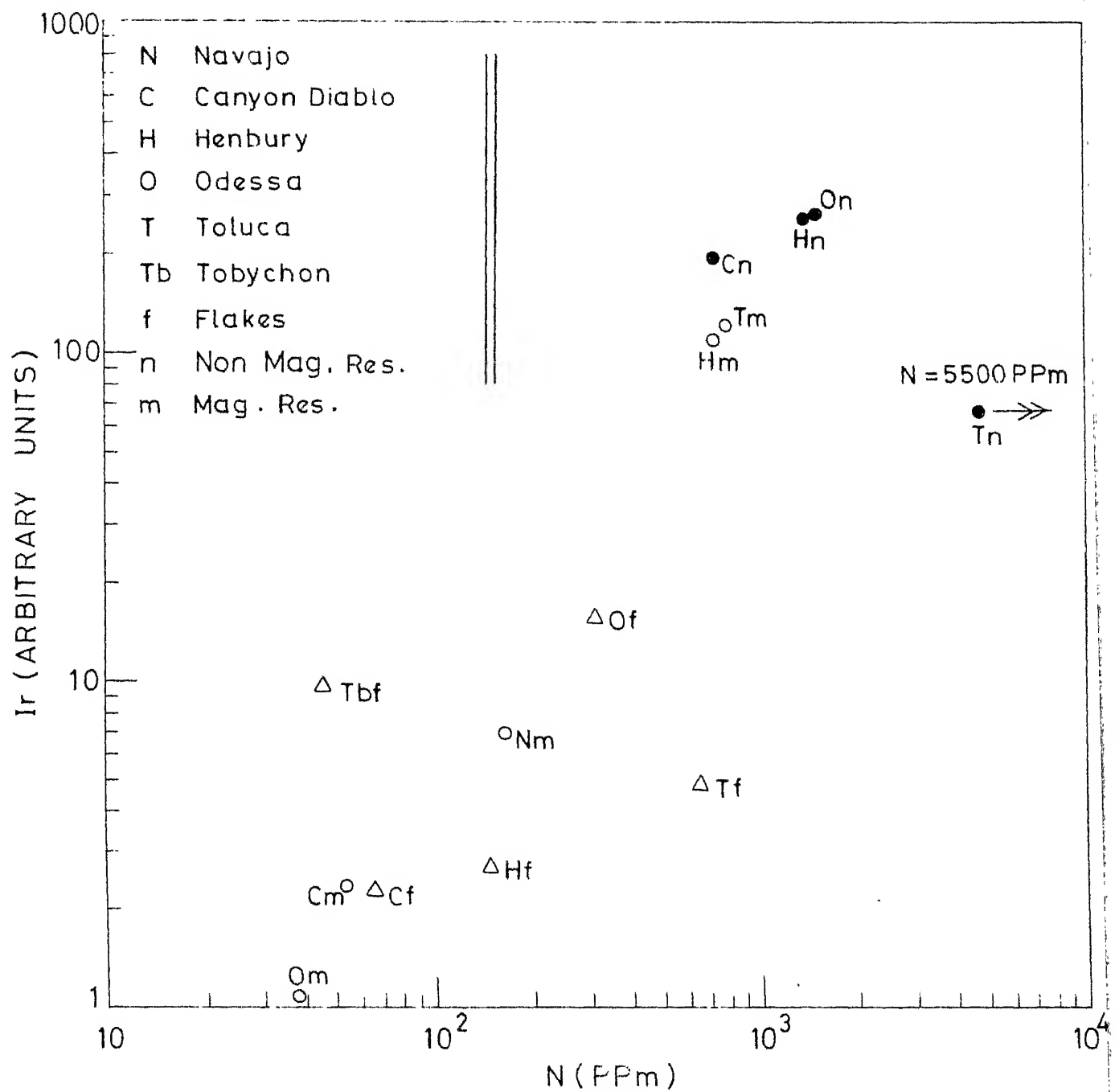
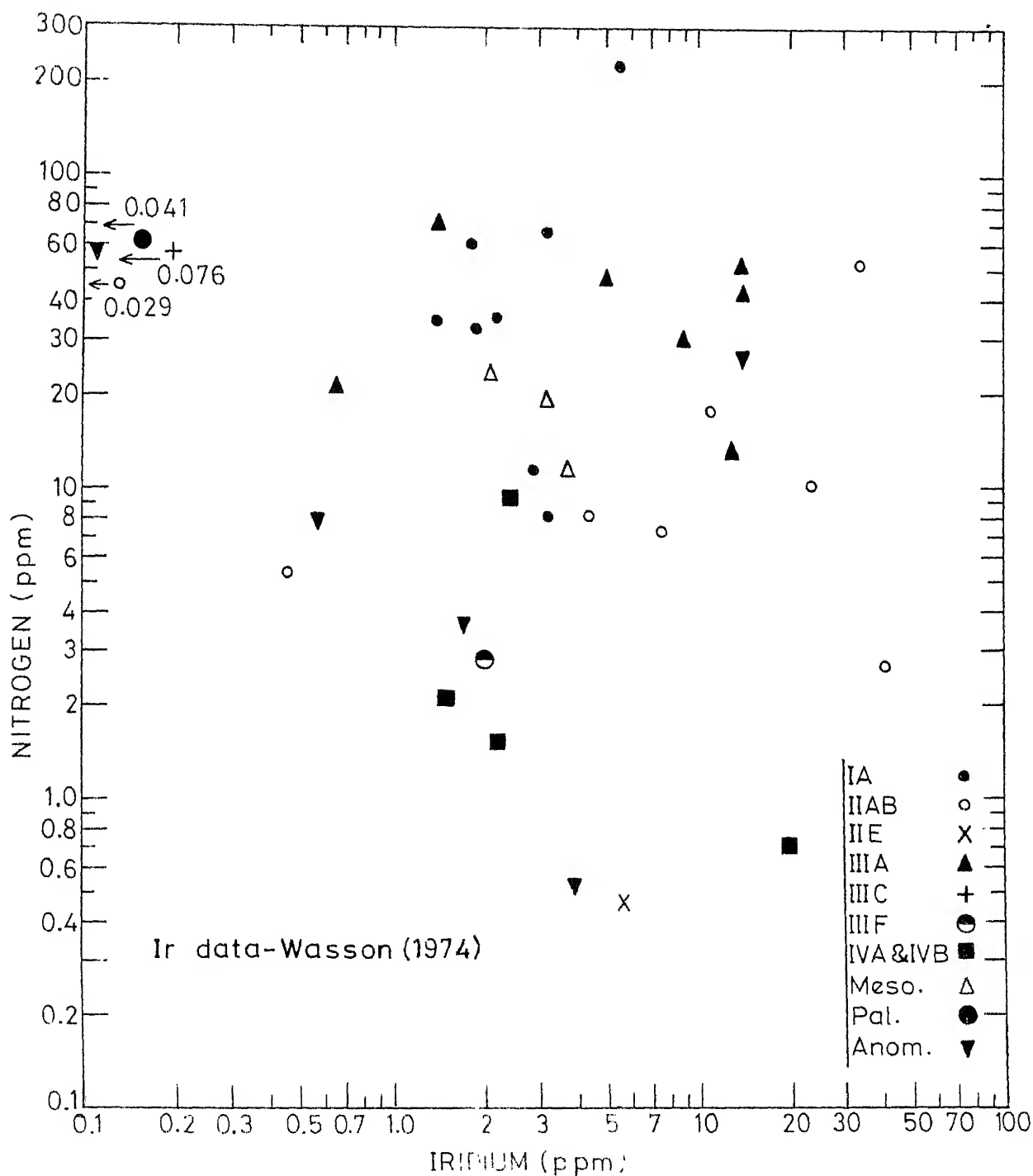Fig. 5.5   N vs. Ir for various Iron meteorite phases.

Fig.5.6   N vs. Ir plot for some irons and stony irons.

meteorites as shown in Fig. 5.6 (from Shukla, 1977) and also
from Table 5.4. The N vs.Ir correlation in the phases speaks
of a common origin for these enrichments. Similar trend is
observed for ^{6}Li also (to be discussed in Section 5.5.3). The
effect of, greater solubulity of N in taenite, and the presence
of CrN in IIIA irons might be insignificant compared to
N enhancement caused by the presence of these grains. Survival
of such grains, having high N content, in iron meteorites,
speak in favour of a cold origin for these meteorites.

5.5.3 Lithium : In all the meteorites studied,^{6}Li is high
in separated phases compared to the bulk. It is possible that
during dissolution of the irradiated piece, ^{3}H got adsorbed on
the surface of the residue and gave high ^{6}Li contents. Our
results on phases separated before irradiation on CD agree
with the other set (except for nmr). This rules out the possi-
bility of our results being experimental artifacts. The ^{6}Li
enrichment in various phases has to be due to ^{6}Li rich grains,
as otherwise ^{3}H should have diffused out. Even from these
grains most of the ^{3}H might have escaped due to its longer
range ($\smallsmile$ 30μ) compared to the grain size. The fact that
such a ^{3}H escape is in fact occurring is demonstrated by the
higher ^{6}Li($\smallsmile$ x 20) in CD nmr irradiated after separation, as
compared to CD nmr from irradiated piece.

When the grains are dispersed in iron matrix, the ^{3}H
produced from ^{6}Li in the grains escapes into iron matrix if the

grain size is smaller than the ^{3}H range ($\backsim$ 30μ for silicate grains). The ^{3}H from iron matrix diffuses out and thereby a low ^{6}Li results. On the other hand, when such grains are irradiated together the ^{3}H that escapes from one grain gets embedded in an adjacent grain and no net ^{3}H loss results. The grain sizes of our terrestrial Li standards BCR-1, W-1, G-2 etc. are within ^{3}H range. But their Li contents determined by our method agree well with those determined by other methods. This agreement testifies that there will be no net loss of ^{3}H when the grains are irradiated together. The work of Montescu and Costea, 1966 on LiCl powder also demonstrated that there will be no net ^{3}H loss.

Grains with such high Li contents might alone account for the Li in iron meteorites. In view of the ^{3}H loss when the grains are dispersed, our ^{6}Li data for bulk meteorites might only represent a lower limit of ^{6}Li contents in iron meteorites. The ^{6}Li contents of the nmr (0.86 ppm for CD and 1.13 ppm for CdC) are much higher compared to the ^{6}Li in bulk silicate inclusions of Odessa (0.10 – 0.15 ppm) (Krankowsky and Müller, 1967). This is another indication that these non-magnetic residues are different from the bulk inclusions. Also similar to N, ^{6}Li shows a positive correlation with Ir, for the residues, as shown in Fig. 5.7. This correlation might have been weakened due to ^{3}H loss problem. The plot of ^{6}Li vs Ir for bulk meteorites looks similar to that N vs.Ir (Fig. 5.6) and displays no relation.
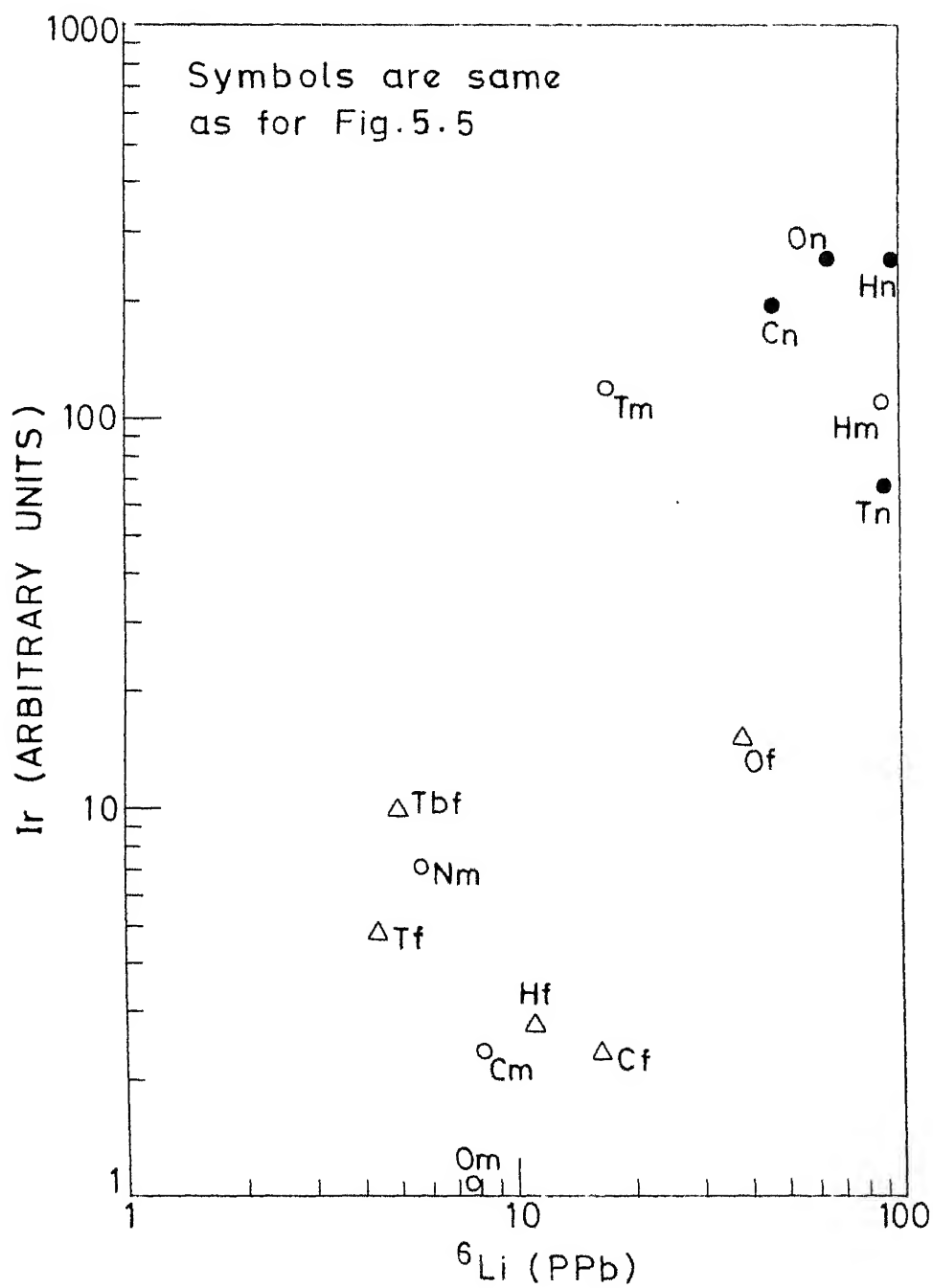
Fig.5.7 ^{6}Li vs. Ir for various Iron meteorite phases.

This is also evident from the data in Table 5.4.

5.6 Xenon in the Residues

Xenon has been measured in the residues of CD and CdC, by Prof. Yu. A. Shukolyukov and Dr. D. Vu. Minh at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow. Some important experimental details, as described by Dr. Minh in a private communication, are given here.

'Samples are wrapped in aluminium foil and degased for 7 hrs. in vacuum at about 200° C. Xe was extracted from the samples in a resistance-heated molybdinum crucible. In order to reduce the blank, the molybdinum crucible was pre-degassed before use. Xe blank was 5×10^{-13} CCSTP ^{136}Xe at 1600° C. Extraction time was $\frac{1}{2}$ hr. at 1600° C. Gases are cleaned using a pair of Ti-Zr getters cooled from 800° C to room temperature. Xe was separated from other noble gases using activated charcoal at dry ice temperature and then admitted to the mass spectrometer.

Xe was analysed statically in the mass spectrometer MN-1201, using an automated data acquisition system with an on-line Hewlett Packard 2821A calculator. Data was obtained by repeated scanning of the mass spectrum by automatic stepping of the magnetic field. Ten complete scans were taken. Isotopic ratio and the concentration of Xe were extrapolated to the time when the gas was admitted to the mass spectrometer. The mass spectrometer sensitivity was maintained with a standard gas

pipette, which delivers known amount of Xe of atmospheric composition. The mass descrimination effect was about 0.2 per mass unit. Appropriate corrections were made for all samples'.

The Xe data are given in Table 5.9. In the same table are also given the Xe isotopic compositions of atmospheric air, solar wind, AVCC, Allende Q and Havero dark inclusion. The data are normalised with respect to ^{130}Xe, because this isotope is not produced either in spallation or in fission. The important features that are apparent from the Xe data are :
1) All the residues are enriched in ^{129}Xe compared to atmosphere presumably due to ^{129}I decay. The enrichment factors vary, the CD mr being the most enriched while the nmr of the same meteorit is the least enriched, out of the samples studied. These enrich- ments are much less than the ^{129}Xe excesses found in bulk inclu- sions of iron meteorites (Alexander and Manuel 1967, 1968).
2) The total Xe of the nmr is higher than the corresponding mr. The enrichment is by a factor of 6 for CD and a factor of 10 for CdC. 3) Both the nmr are depleted in the isotopes 124 and 126 whereas a clear excess of these isotopes is evident for mr (due to spallation?) relative to atmospheric Xe. 4) The Xe isotopic compositions of the residues do not match with any of the Xenons given in Table 5.9. The comparisons will be better appreciated on relative deviation plots. The relative devia- tions, for an isotope i normalized to isotopes X, with respect to standard is given by

Table:5-9 Xenon in Separated Phases of Iron Meteorites

$^{130}Xe = 1.000$

Sample	Wt. mg.	Release Temp. (°C)	$^{130}*Xe$	124	126	128	129	130	131	132	134	136
Canyon Diablo Non Mag.Res.	14.5	1600	1.356	0.0203 +.001	0.0186 .0022	0.4756 .005	6.608 .005	1.000	5.186 .040	6.544 .055	2.646 .025	2.212 .073
Canyon Diablo Mag.Res+Flakes	179.0	1600	0.226	0.029 .0008	0.025 .0008	0.466 .0066	7.902 .042	1.000	5.263 .0338	6.557 .030	2.525 .018	2.119 .009
Campo del Cielo Non Mag.Res.	27.0	1600	1.880	0.0210 .0009	0.0213 .0007	0.456 .0048	7.097 .040	1.000	5.176 .026	6.602 .034	2.574 .017	2.174 .009
Campo del Cielo Mag.Res.	119.5	1600	0.186	0.0229 .0009	0.0240 .0011	0.483 .0054	6.964 .060	1.000	5.324 .040	6.669 .060	2.666 .026	2.207 .014
Air[1]				0.0235	0.0220	0.470	6.480	1.000	5.192	6.592	2.559	2.175
Solar wind[1]				0.0289	0.0259	0.5036	6.351	1.000	4.986	6.060	2.239	1.817
AVCC[1] (Trapped)				0.0278	0.0251	0.4963	6.319	1.000	5.018	6.135	2.300	1.889
Allende[2] (3Cl)				0.0293 .0005	0.0255 .0003	0.506 .0046	7.077 .070	1.000	5.085 .056	6.215 .046	2.443 .022	2.102 .020
Havero[3] Dark Inc.				0.03437	0.02875	0.5437	6.625	1.000	5.169	6.250	2.419	2.075

1.Srinivasan and Anders 1978; 2.Lewis et al., 1975; 3.Weber et al., 1971

* In $(10^{-10}$ CCSTP/g)

$$g_X^i = (i/X)_{sample}/(i/X)_{standard}$$

g_{130}^i values with respect to atmosphere and Allende Q are calculated for the residues and are given in Table 5.10. These g_{130}^i values are plotted vs. i in Fig. 5.8 (with respect to atmosphere) and in Fig. 5.9 (with respect to Allende Q). For comparison purposes the g_{130}^i for solar wind AVCC, Allende Q and Hävero dark inclusion (all with respect to atmosphere) are plotted in Fig. 5.10. Comparison of Fig. 5.8 and Fig. 5.10 indicates the following points : All well known components of Xe are enriched in light isotopes and depleted in heavy isotopes, with respect to atmosphere, which has the most fractionated Xe known. In contrast, both nmr are very much depleted in the light isotopes 124 and 126 with respect to atmosphere while the mr of CD is almost similar to Allende Q and Hävero inclusion. The mr of CdC is like that of the mr of CD but for the isotope 124, which is depleted. This may be due to some contamination from non-magnetic material that is embedded in it. Such light isotope depletions in Xenon, observed here for nmr are not known in any terrestrial or meteoritic materials. Fig. 5.9 shows the similarity between both nmr and both mr (except for the point 124) with respect to Allende Q. In all four cases the heavy isotope 136 and the light isotopes 124, 126 and 128 are depleted with respect to Allende Q. For both the nmr the decrease is monotonic (except for the isotope 136). These comparisons indicate a strange Xe component in the residues.

Table:5-10 q^i_{130} Values with respect to atmosphere /or Allende Q of various samples

| Sample	w.r.t	124	126	128	129	130	131	132	134	136
Canyon Diablo Non Mag.Res.	Atmosphere (1)	0.846 +.042	0.857 .101	1.008 .01	1.015 .008	1.000	0.992 .008	0.989 .008	1.030 .009	1.013 .033
	Allende Q (2)	0.693 .036	0.729 .086	0.940 .013	0.933 .012	1.000	1.020 .013	1.053 .012	1.083 .014	1.052 .036
Canyon Diablo Mag.Res+Flakes	1	1.208 .003	1.152 .036	0.987 .014	1.214 .006	1.000	1.007 .006	0.990 .004	0.984 .007	0.970 .004
	2	0.990 .032	0.980 .033	0.921 .015	1.116 .012	1.000	1.035 .013	1.055 .009	1.033 .012	1.008 .01
Campo del Cielo Non Mag.Res	1	0.875 .036	0.981 .030	0.966 .010	1.09 .006	1.000	0.990 .005	0.997 .005	1.003 .007	0.996 .004
	2	0.717 .032	0.835 .028	0.901 .012	1.003 .011	1.000	1.018 .012	1.062 .009	1.054 .012	1.034 .010
Campo del Cielo Mag.Res.	1	0.954 .037	1.106 .050	1.023 .011	1.070 .009	1.000	1.018 .008	1.008 .009	1.038 .01	1.010 .006
	2	0.781 .033	0.941 .044	0.954 .014	0.984 .013	1.000	1.047 .014	1.073 .012	1.091 .014	1.050 .012
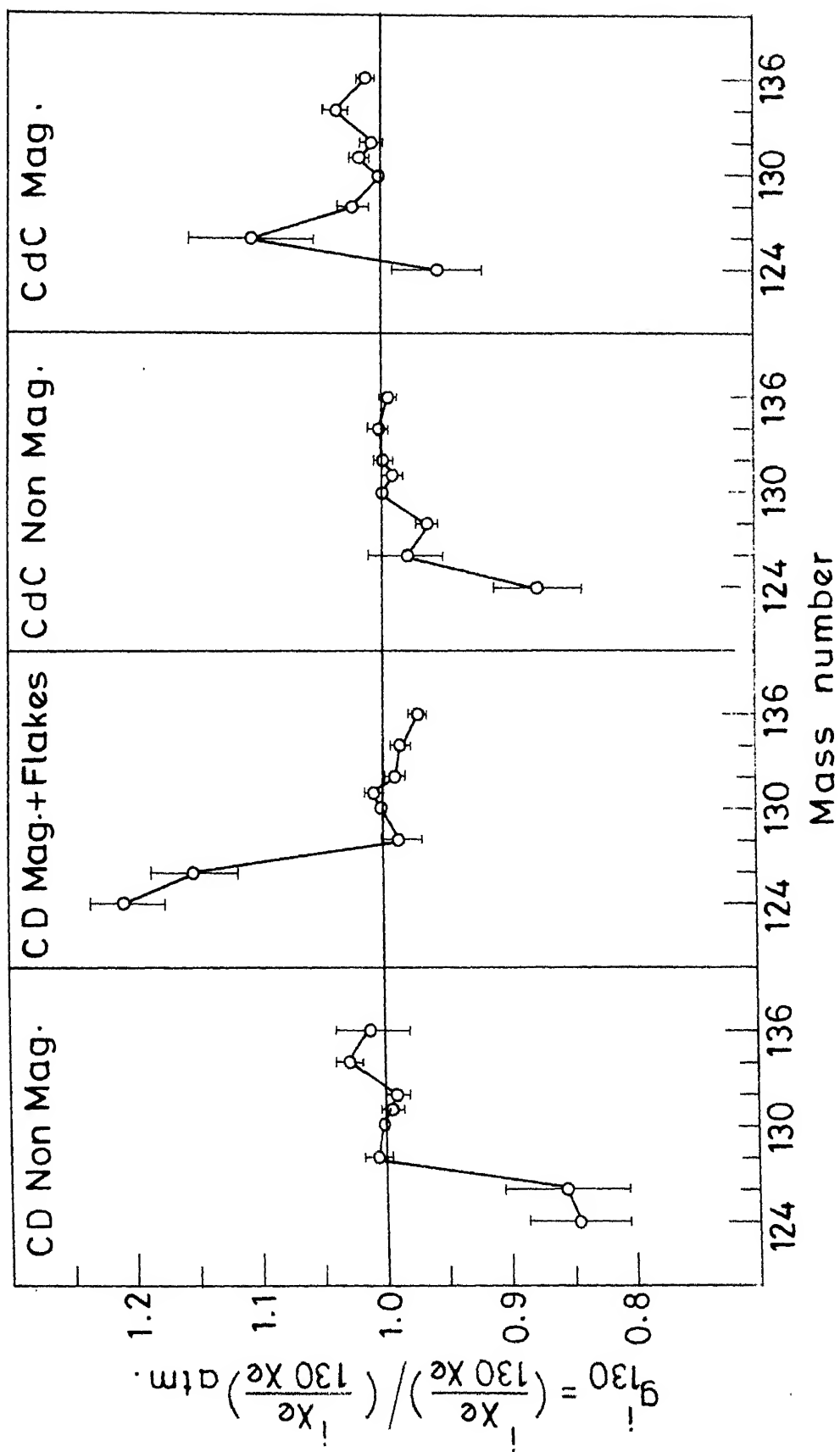
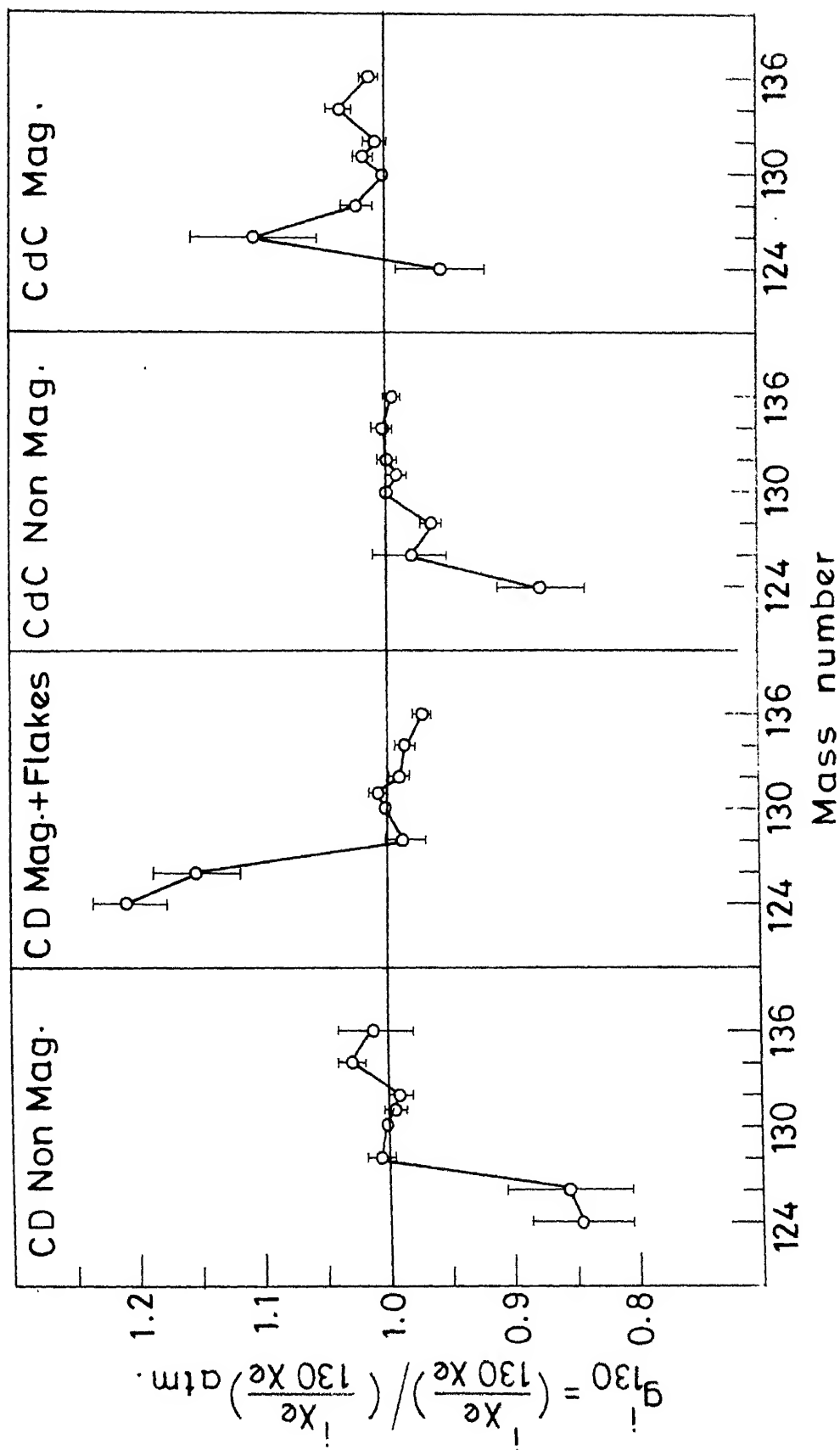Fig. 5.8 g^i_{130} with respect to atmosphere for Xe in the residues.

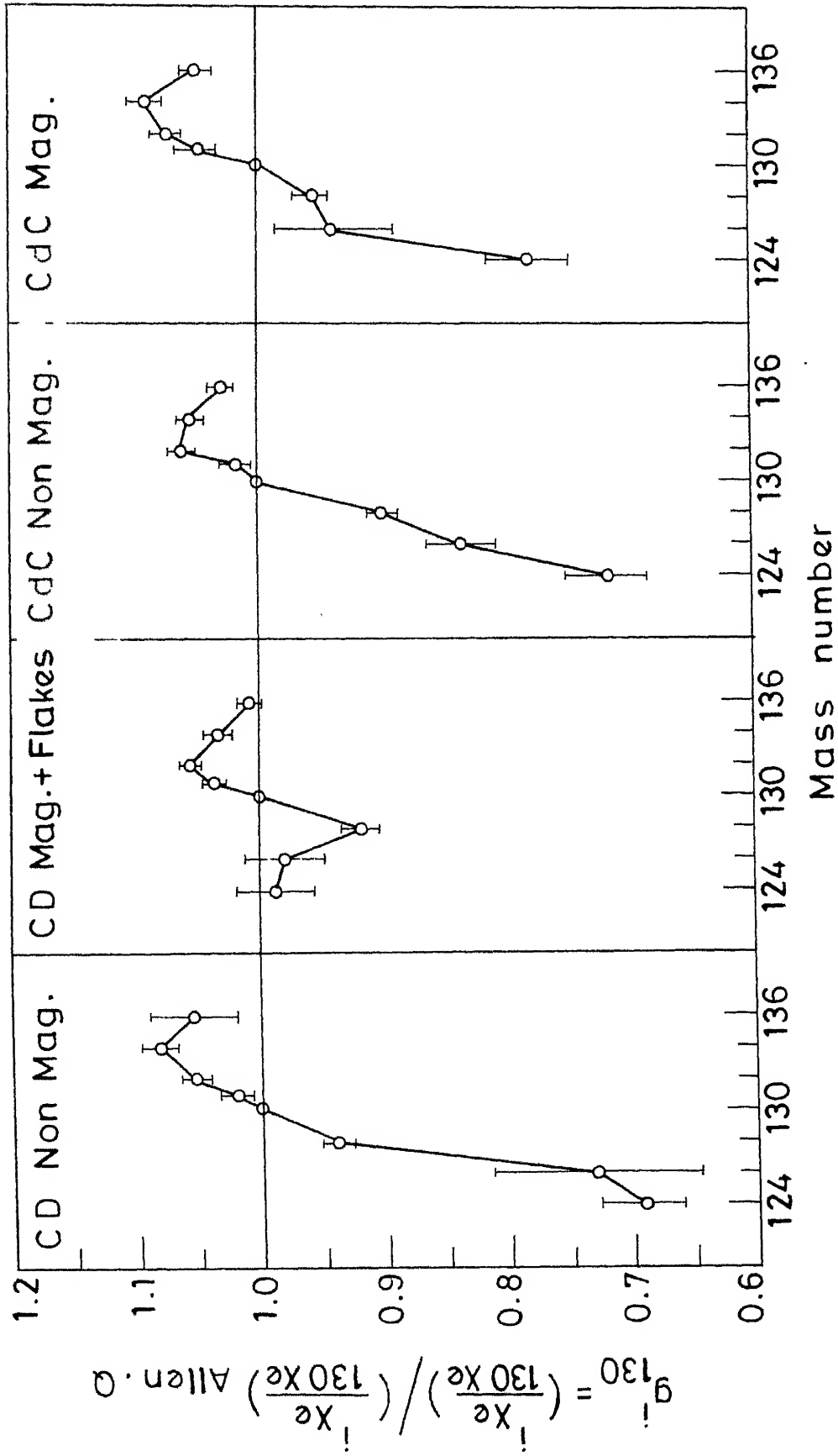Fig. 5.8 g^i_{130} with respect to atmosphere for Xe in the residues.

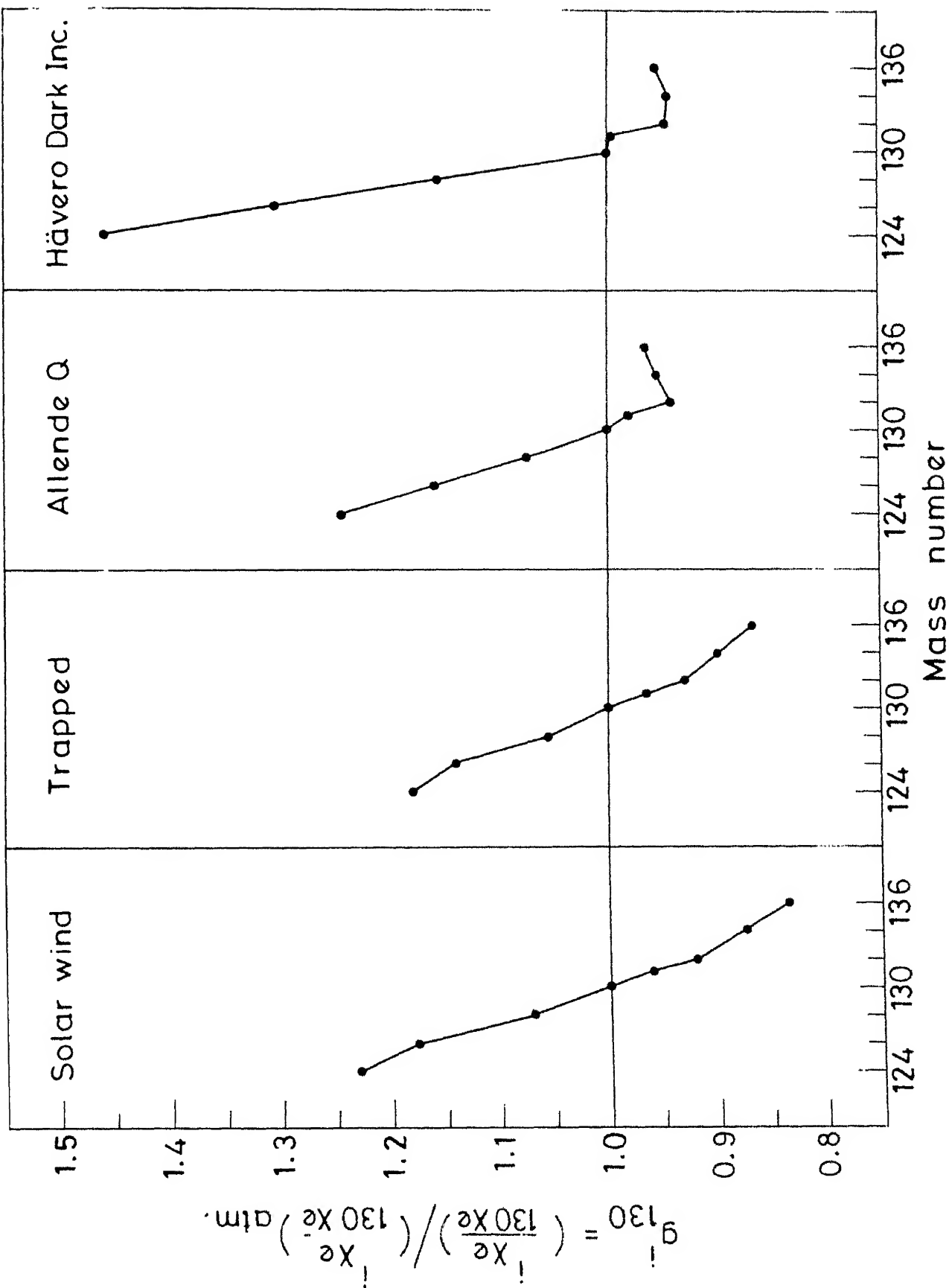Fig. 5.9 g_{130}^i with respect to Allendo Q for Xe in the residues.

$$g_{130}^i = \left(\frac{{}^i Xe}{{}^{130} Xe}\right) \bigg/ \left(\frac{{}^i Xe}{{}^{130} Xe}\right)_{Allen.Q}$$

Fig.5.10 g_{130}^i with respect to atmosphere for some Xenons.

$$g_{130}^i = \left(\frac{{}^i Xe}{{}^{130} Xe} \right) \Big/ \left(\frac{{}^i Xe}{{}^{130} Xe} \right)_{atm.}$$

Atmospheric contamination is possible and will be more serious for Xe in particular. The adsorbed Xe can be released even at 900°C (Niemeyer and Leich, 1976). In our samples atmospheric contamination is negligible as evidenced by the following facts : 1) There is no Xe release prior to 1200°C (Dr. Minh, private communication), 2) Atmospheric contamination, if present would have diluted the light isotope depletions found, as atmospheric Xenon is enriched in these isotopes.

The Xe of nmr does not match with any of the so many Xe components known to be present in stone meteorites (reviewed in Chapter 1). Similar depletion of light isotopes (78,80) has been found for Kr in an Allende carbonaceous residue (Frick, 1977). Other than this there is no report of light isotope depletion for a noble gas (^{22}Ne is a special case).

Earlier Xe measurements, in inclusions of iron meteorites, have shown certain anomalous features (reviewed in Chapter 1) but a behaviour of this sort was not found. Only a step-wise heating experiment can reveal the exact nature of this 'strange' Xe component. At the moment it can only be said that the Xe in the nmr is 'strange'. Until the exact composition of the strange component is known, it is unwise to predict the possible origins.

5.7 Osmium in the Residues

The high Ir in the non-magnetic residues shows the presence

of metal grains, probably of primordial origin. Such grains should be highly enriched in Os as well (Blander et al., 1980). In view of the anomalous Xe in these residues, it is possible that these metal grains have a presolar (supernova) origin. If it were true we should expect anomalous Os also in these residues. Os has the highest condensation temperature of $1945^{\circ}K$ (Grossman and Larimer, 1974) and as such Os grains should exist in the region of temperature $< 1740^{\circ}K$ where the other carriers of anomalous matter (Al_2O_3 for oxygen anomaly) condense. Also ^{184}Os is produced only in p-process, ^{192}Os only in r-process and ^{190}Os is produced in similar proportions in both s-and r-processes. $^{184,192}Os$ are thus formed in different and distant locations from ^{190}Os. If these interstellar Os grains from different locations were incorporated in the primordial metal grains, then the ratios 184/190 and 192/190 might be expected to be several tens of % different from terrestrial values. With this idea, Grossman and Ganapathy, 1976 have studied Os in two Allende inclusions known to have anomalous oxygen but found the isotopic ratios to be within $\pm 2\%$ of the terrestrial value. These authors have concluded that the metal Os condensed from an isotopically homogenized gas either in presolar nebula or from solar nebular vapour.

If CCFXe is due to supernova r- and p-processes, it should be accompanied by Os also with different r-and p-isotopes. With this view, Takahashi et al., 1976 searched for Os

anomaly in the Allende residues, which carry the CCFXe, but
found normal Os. Takahashi et al., 1976 concluded that the
stellar source of the anomalous O and Mg did not synthesize
heavier elements.

We wanted to verify if Os is anomalous in our residues.
A radiochemical procedure is followed, the details of which
are described in Chapter 1. Unfortunately, there was no Os
standard in this set of irradiations as we did not plan to
analyse for Os a priori. We can, therefore, neither give the
absolute Os value nor the direction of the anomaly. We can
present the data relative to one of the residues. The activity
ratios of 191/185 after normalizing to a common zero time are
given in Table 5.11. Also given in this table are the ratio of
the Os activity in the nmr with respect to mr for both the
meteorites CD and CdC. The nmr of CD is enriched in Os, similar
to Ir. But for nmr of CdC, Os is depleted as compared to Ir.
Here we have assumed complete recovery of Os as the yield was
not determined. If recovery factors are also considered, then
the Os enrichments of nmr may be similar to Ir enrichments. The
enrichment of Os also, as expected, confirms the presence of
primordial metal grains in the nmr.

The isotopic ratios of CdC are plagued by large errors
because of week activities, but they are similar to their
respective counterparts of CD. The 191/185 ratios of the nmr
and mr of CD differ outside their error range. The difference

Table 5.11 Activity ratio of $^{191}Os/^{185}Os$ in
separated phases of iron meteorites

Sample	$^{191}Os/^{185}Os$	Error (%)	$\dfrac{Os(non\text{-}mag.)}{Os(mag.)}$ w.r.t ^{191}Os	w.r.t ^{185}Os
Canyon Diablo				
Mag.Res.	6.59 ± 0.105	1.6	133	126
Non-mag.Res.	6.04 ± 0.024	0.4		
Campo del Cielo				
Mag. Res.	6.51 ± 0.145	2.23	0.48	0.52
Non-mag.Res.	· 6.25 ± 0.38	6.08		

with respect to nmr is 9.1 ± 1.8 % (at 1σ level). These ratios

are represented in Fig. 5.11. It might be that a similar trend

in CdC nmr is masked by errors. This result gives an indication

that the non-magnetic residues have anomalous Os compared to the

magnetic residues. This result will have lot of implications

in view of the indicated presence of primordial metal grains

in these residues. If this result were true, then the presence

of 'presolar' grains can explain all the anomalies found (High

N, Li, Ir, Os and Xe; the anomalous Xe and Os, presence of free

radicals and organic compounds) in the non-magnetic residues.

Repeat experiments to confirm this result are in progress.

5.8 Implications for the Origin of Iron Meteorites

Though nmr of high N and Li are shown to be present in

other than IA irons also, in view of the fact that the rest of

the aspects are studied in only IA irons, we restrict ourselves

to see the implications for the origin of IA iron meteorites.

Several features suggest that group IA irons are different

from the rest in their mode of origin. The presence of silicate

inclusions with angular shapes and chondritic features suggest

that these meteorites have not undergone, extensive heating

and hence cannot be core products of large parent bodies. To

incorporate these features and also that of the correlation of

I-Xe ages with Ni content (Niemeyer, 1979b);Wasson et al., 1980

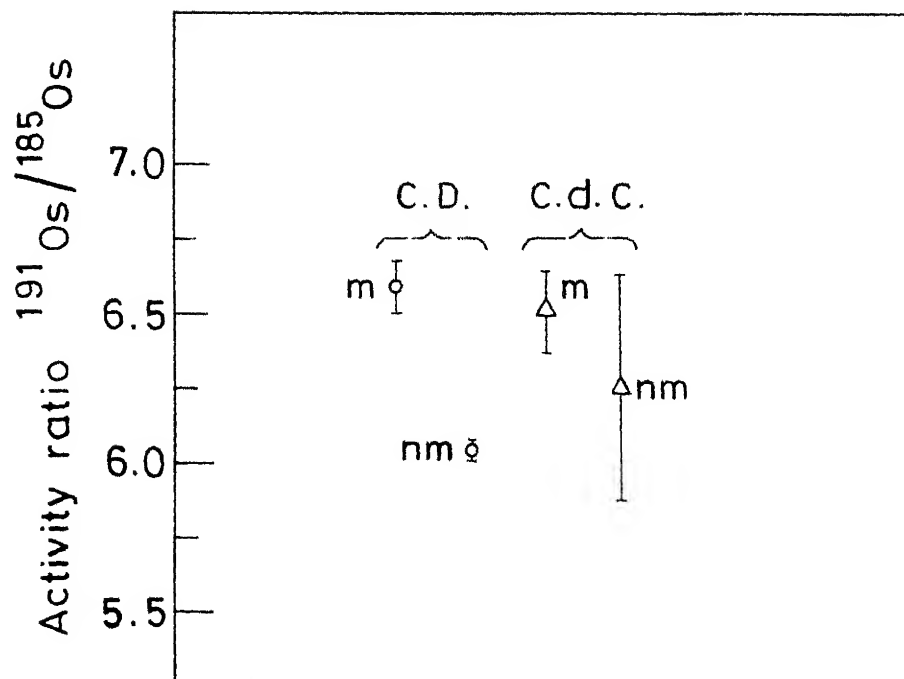have proposed that the IA irons (and also III CD) have formed

Fig. 5.11　Activity ratios of Os for the residues.

in local melt pools of mega-regoliths of chondritic parent
bodies. But all these features and also the presence of
anomalous grains might be well explained if IA irons (and
most probably many other groups also) have condensed directly
from the solar nebula, may be in a process similar to the one
envisaged by Arrhenius and Alfven, 1971.

Sears, 1978b suggested that the major iron meteorite
groups can be condensed directly around 600-700°K, but at
varying pressures. In particular he suggested that IA irons
must have agglomerated from grains which condensed at lowest
temperature and highest pressure (10^{-5} - 1 atm.). In such a
scenario, the condensing grains must have trapped the anomalous
grains floating around. As anomalies in noble gases and other
elements are being reported in all classes of chondrites, it is
not surprising that anomalous grains are available at the site
of formation of IA irons. If this is true, iron meteorites
better preserve these grains compared to stones, where the
dilution is larger. This explains the ease with which such
anomalous grains can be isolated (simple acid dissolution, and
a magnetic separation in our case) from irons as against the
elaborate procedures of selective leaching etc. employed for
stone meteorites.

Presence of such grains can explain some of the as yet
unexplained puzzles of IA irons. The excess K-Ar ages might be
due to excess ^{40}Ar carried by these grains. Such ^{40}Ar carrying

grains have been proposed by Jessberger et al., 1980 to account for the excess K-Ar ages of Allende inclusions. The enrichment of light carbon in the residues (Deines and Wickman, 1973) and all our anomalous results might then be accounted for by the presence of these 'presolar' grains. The source regions of these grains can only be predicted after detailed isotopic studies. Isotopic studies on N,Li, Os, Te and step-wise heating studies for Ar, Kr and Xe will definitely throw light on the locals for these anomalous grains. Probably some of the anomalies (C and Xe) are caused by the associated physical effects during condensation. Some isotopic studies are under way.

5.9 Suggestions for Future Work.

If our idea of the existence of 'presolar' debris in iron meteorites is correct, of course, a new area will be open for extensive studies. Of immediate importance is to confirm the Os results and to identify the nature of Xe anomaly. Isotopic studies on N,Li,Te and other noble gases will enable to identify the nature of these grains. This type of search should be conducted in all iron meteorite groups, as the presence of these grains has lot of implications on their mode of formation.

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